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AMERICAN LEATHER CHEMISTS ASSOCIATION

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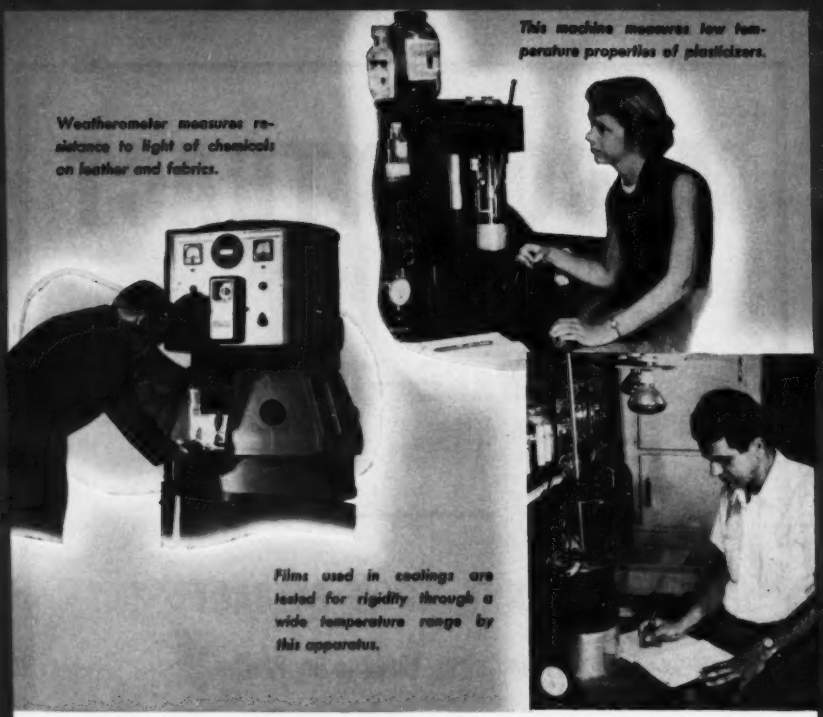
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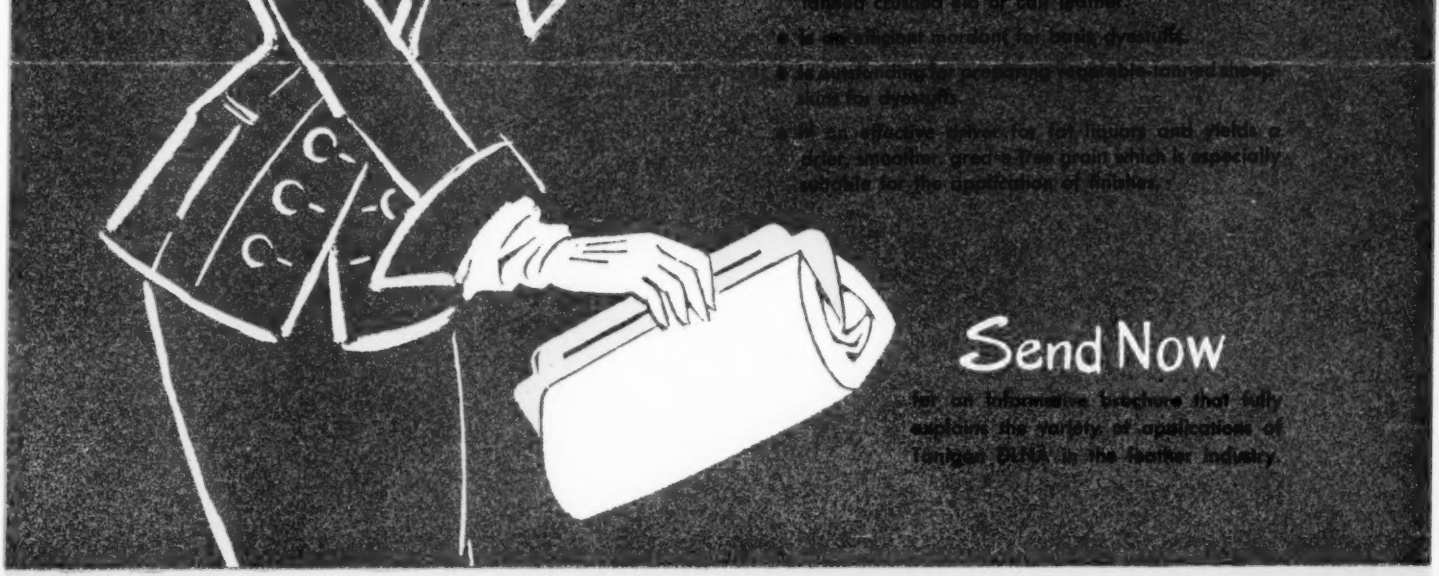

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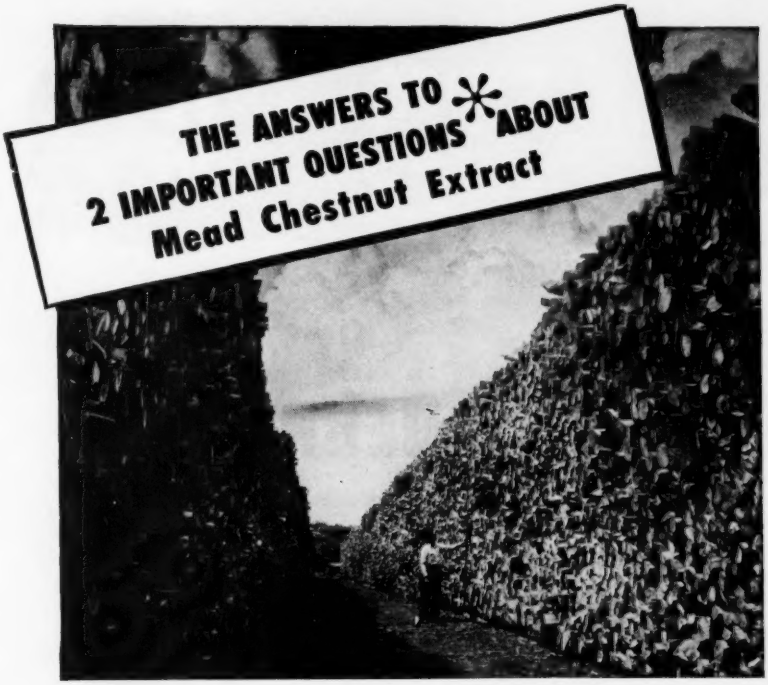

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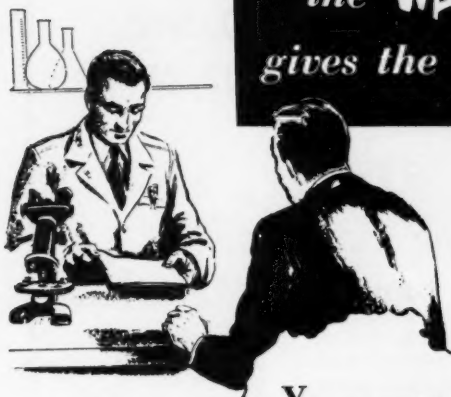

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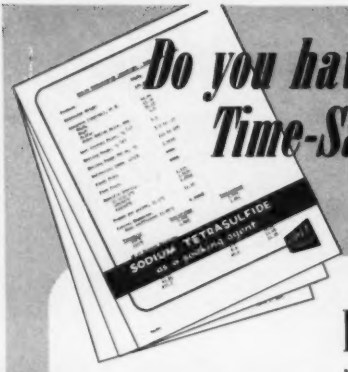

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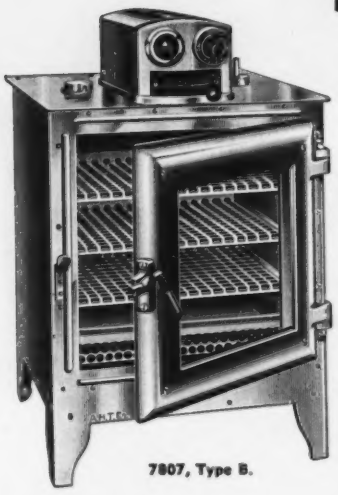

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Methods for the Analysis of Vegetable Tanning Materials

ANALYSIS OF VEGETABLE TANNING MATERIALS—GENERAL (A1)

1. SCOPE

1.1 These methods are intended for use in the chemical analysis of vegetable tanning materials.

2. SAMPLES AND SPECIMENS

2.1 The preparation of the composite sample of a vegetable tanning material, from which specimens are to be taken for analysis, shall be as described in Method J10.

3. APPARATUS AND REAGENTS

3.1 All volumetric glassware used in the chemical analysis shall comply with the specifications for Class B of Federal Specification DD-V-581, Volumetric Apparatus, Glass.

3.2 Unless otherwise specified, all reagents used in the chemical analysis shall comply with specifications recommended by the Committee on Analytical Reagents of the American Chemical Society.

3.3 The distilled water used in the chemical analysis shall have a pH of not less than 5.5 nor more than 7.0 and shall give a residue of not more than 0.0005 g. when 100 ml. is evaporated and dried in a platinum dish.

3.4 General laboratory apparatus and reagents shall be available. (Special apparatus and reagents are described in the individual methods.)

4. PROCEDURE

4.1 All funnels, collecting dishes and other apparatus used during the analysis shall be covered with suitable covers so as to prevent, or reduce to a minimum, any change in concentration of solutions by evaporation of water.

4.2 All aliquots of analytical solutions, pipetted for the determination of total solids, soluble solids, nontannins, or other, shall be measured at the same temperature.

5. GENERAL ANALYTICAL PROCEDURE FOR THE ANALYSIS OF VEGETABLE TANNING MATERIALS

5.1 Sampling of Vegetable Materials Containing Tannin. . . . (Method J10)
5.2 Extraction of Raw and Spent Materials. . . . . (Method A5)
5.3 Moisture in Raw and Spent Materials . . . . . (Method A6)
5.4 Preparation of Solutions of Liquid Extracts . . . . . (Method A10)

5.5 Preparation of Solution of Solid, Pasty and Powdered Extracts ..... (Method A11)
5.6 Cooling of Analytical Solutions..... (Method A12)
5.7 Evaporation and Drying of Analytical Solutions..... (Method A13)
5.8 Total Solids and Water ..... (Method A20)
5.9 Soluble Solids and Insolubles..... (Method A21)
5.10 NonTannins and Tannin ..... (Method A22)
5.11 Analysis of Tannery Liquors..... (Method A25)
5.12 Sugar in Tanning Materials..... (Method A30)
5.13 Color Tests with Sheepskin Skiver ..... (Method A40)
5.14 Lignosulfonates (Sulfite Cellulose) ..... (Method A50)
5.15 Official Certification (Official Forms for Reporting Analyses of Extracts and Raw and Spent Materials).... (Method A60)

A.L.C.A. Provisional Method February 1954

SAMPLING OF VEGETABLE MATERIALS CONTAINING TANNIN (J10)

1. SCOPE

1.1 These methods are intended for use in obtaining representative samples of Vegetable Materials containing Tannin.

1.2 Samples are taken for the purpose of having representative quantities of economical and convenient size from a lot, or from sections of a lot, of material for examination and test, so that agreement may be reached with regard to:

A. The extent of variation of quality in different portions of the lot.

B. The average quality of the whole lot of material.

1.3 No directions for sampling, however explicit, can take the place of judgment, skill, and previous experience on the part of persons actually engaged in the sampling or the supervision of the sampling. These directions are intended to supplement that experience and, particularly, to serve as a guide in the selection of the method which is to be used, in common, by each of two or more contracting parties.

1.4 Tanning materials contain moisture in varying amounts, depending both on the nature of the material and on the climatic conditions, so that sampling must be carried out as quickly as is consistent with thoroughness in order to avoid changes in moisture content.

2. NUMBER OF PACKAGES TO BE SAMPLED

2.1 The number of packages to be sampled from any given lot of tanning material composed of solid, powdered or pasty extract, crude or manufactured tanning materials, in bales, boxes, bags, barrels, or similar packages, shall be as shown in the following table and shall be selected from as uniformly distributed parts of the lot as is possible at the time of weighing.

Number of Packages in Lot	Number of Packages to Be Sampled	Number of Packages in Lot	Number of Packages to Be Sampled	Number of Packages in Lot	Number of Packages to Be Sampled
1–3	each	1201–1300	25	4551–4700	48
3–24	3	1301–1400	26	4701–4900	49
25–40	4	1401–1510	27	4901–5100	50
41–60	5	1511–1640	28	5101–5300	51
61–84	6	1641–1730	29	5301–5520	52
85–112	7	1731–1860	30	5521–5720	53
113–144	8	1861–1980	31	5721–5940	54
145–180	9	1981–2100	32	5941–6160	55
181–220	10	2101–2240	33	6161–6380	56
221–264	11	2241–2380	34	6381–6600	57
265–312	12	2381–2520	35	6601–6840	58
313–364	13	2521–2660	36	6841–7080	59
365–420	14	2661–2810	37	7081–7320	60
421–480	15	2811–2960	38	7321–7560	61
481–544	16	2961–3120	39	7561–7800	62
545–612	17	3121–3280	40	7801–8060	63
613–684	18	3281–3440	41	8061–8320	64
685–760	19	3441–3610	42	8321–8580	65
761–840	20	3611–3780	43	8581–8840	66
841–920	21	3781–3960	44	8841–9120	67
921–1010	22	3961–4140	45	9121–9400	68
1011–1100	23	4141–4320	46	9401–9660	69
1101–1200	24	4321–4550	47	9661–10000	70

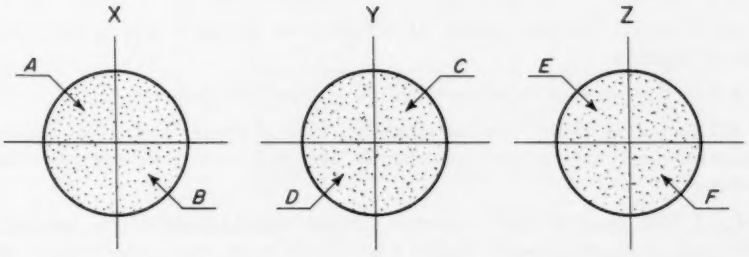
2.1.1 Where a shipment exceeds 10,000 packages, it shall be divided into as few, equal, sections (of not more than 10,000 packages each) as possible and each section shall be sampled and analyzed as if it were an individual shipment. In such case, the mean of the analyses of the sections shall constitute the analysis of the shipment.

3. QUARTERING SAMPLES

3.1 "Quartering" is a term applied to the following method of reducing the size of samples without impairing their representative quality:

3.1.1 All of the material, taken from the various containers or parts of the shipment of solid material being sampled, shall be immediately and thoroughly mixed on a square piece of (11 oz.) canvas. In the case of solid

extracts, large pieces shall have been broken previously so as to pass a screen having round openings one-half inch in diameter (par. 6.3). The pile shall be divided into 4 equal portions, as in diagram X, and quarters *A* and *B* shall be discarded. The remaining two quarters shall then be remixed thoroughly, again divided into 4 equal portions and quarters *C* and *D* (diagram Y) discarded. This process shall be repeated until the mixture of any two remaining quarters of the sample be of sufficient size to secure the individual samples as specified below:



The two remaining quarters shall then be thoroughly mixed and divided into as many uniform sections as necessary, so that each section will be large enough to fill one of the required number of containers. All fine, powdery material in each section shall be completely removed with its respective section, whether the section is discarded or placed in a sample container.

4. FILLING CONTAINERS

4.1 Immediately after the final samples are obtained, they shall be put into clean, dry containers, closed air-tight, sealed, and labeled as described in par. 7.11.

4.2 Liquid and powdered extracts and liquor samples shall be put into stoppered glass bottles of the required size.

4.3 Solid and pasty extracts shall be wrapped in aluminum foil and put into Mason-type jars or tin cans of the required size.

4.4 Cut bark, fruits, roots, galls, nuts, leaves, etc., and spent materials, shall be placed in lacquered, pressed-top tins of the required size, which close air-tight. Boxes or bags must not be used as containers.

4.5 Sample containers shall be of no greater capacity than will conveniently be filled by the sample taken.

5. NUMBER OF SAMPLES

5.1 In addition to the representative samples for submission to the contracting parties, at least one extra sample shall be taken and held in reserve by the sampler, in case one of the regular samples is lost or damaged.

6. APPARATUS

THE APPARATUS SHALL CONSIST OF THE FOLLOWING:

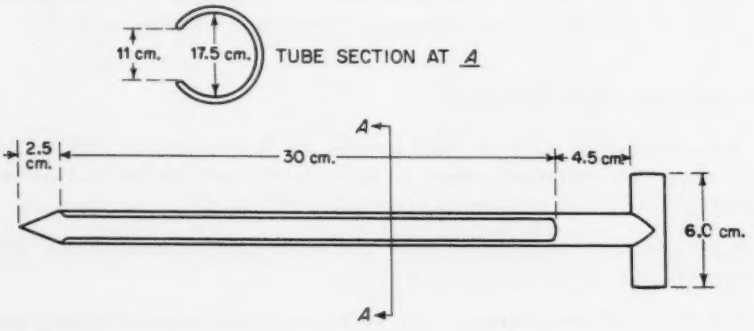
6.1 A balance which will weigh to an accuracy of 10 g.

6.2 Canvas: 11-ounce weight, of sufficient size for use in mixing and quartering samples.

6.3 A sieve having round openings one-half inch in diameter.

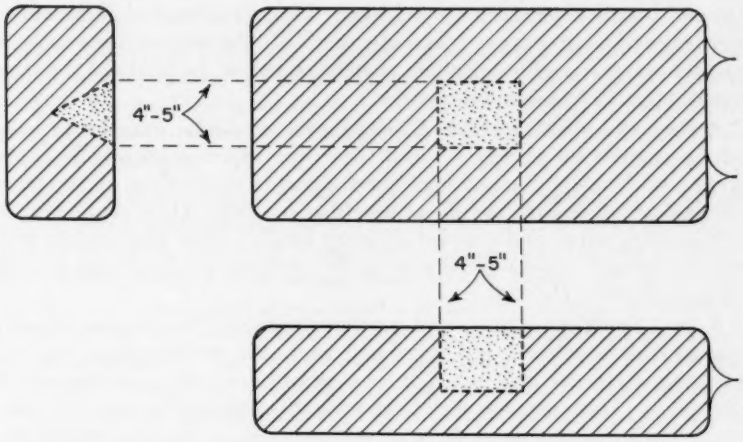
6.4 Sampling Tool: This tool shall be made of brass or other corrosion-resistant metal tubing, with solid handle attached, similar to that described below.

6.4.1 Thin brass or other corrosion-resistant metal tubing, 37 cm. long and 17.5 mm. diameter, is used. A solid steel handle, 6 cm. long, is welded to one end of the tube. A section 11 mm. wide and 30 cm. long is cut out of the side of the tube and the edges of this opening sharply beveled. The working end is cut to a sharp point for piercing sacks, or other tough materials, like plantation gambier.



7. PROCEDURE

7.1 *Solid Extracts.* A suitable, triangular opening shall be cut in the middle of the exposed side of the package to be sampled. A V-shaped wedge, 4 to 5 inches in width on the surface of the exposed side of the package, as near to the middle as possible and to the depth shown in the diagram, shall then be cut out:



This piece shall be removed, including any dry or crumbly exterior portion of it, placed on the quartering canvas and covered to prevent loss of moisture. The V-shaped samples from all the selected packages shall be promptly broken to a size which will pass the sieve (par. 6.3). The mixture shall be quartered and sampled as under par. 3. Each final sample shall weigh approximately 8 ounces and shall be packaged as described under par. 4.3.

7.2 *Powdered Extracts.* A portion shall be drawn from each of the specified number of bags, using the tool described in par. 6.4. The bags shall lie horizontally, with the narrow side exposed, and the sampling tool inserted into the middle of the exposed side and to the center of the bag. The portions removed shall be of equal quantity, shall be thoroughly mixed, and the mixture quartered and sampled as under par. 3. Each sample shall weigh approximately 6 ounces and shall be packaged as under par. 4.2.

7.3 *Barks, Roots, Galls, Nuts, etc., in Bags.* Samples shall be drawn as under "Powdered Extracts" (par. 7.2), using a scoop, when necessary, instead of the sampling tool. The portions shall be thoroughly mixed and the mixture quartered and sampled as under par. 3. Each sample shall consist of enough to fill a one-gallon container, at least, and shall be packaged as under par. 4.4.

7.3.1 In sampling Valonia cups and beards, 3 portions shall be taken from each of the specified number of bags, one from the middle, one midway between the middle and one end, and the third between the middle and the other end. The mixture shall be quartered, etc., as under par. 7.3.

7.3.1.1 In case of disagreement, or when agreed upon between buyer and seller, the following method may be used: The specified number of bags shall be screened through the sieve (par. 6.3) in their entirety and the percentage of

cups and beards determined by weighing. Samples of each shall be drawn by mixing and quartering, etc., as under par. 7.3. The relative proportions of cups and beards, found by weighing, shall be stated on the label and the same proportions shall be taken for analysis.

7.4 *Bark and Wood in Bales.* Chopped bark or similar material in bales shall be sampled by cutting a 6-inch slit in the approximate middle of the covering of the bale. Using a meat-hook about 10 inches long, the material shall be dug out through the slit as deeply as possible. These portions shall be thoroughly mixed and sampled as under par. 3. Each final sample shall consist of enough material to fill a one-gallon container, at least, and shall be packaged as under par. 4.4.

7.5 *Bark and Wood in Sticks or Logs, Bulk Shipment.* The required number of pieces shall be selected and sawed or broken into smaller pieces, each representing in relative size, as nearly as is practicable, the piece from which it was taken. These portions shall be thoroughly mixed and sampled as under par. 3. Each final sample shall be of sufficient size to fill a one-gallon container, at least, and shall be packaged as under par. 4.4.

7.6 *Wood as Chips (from Chipper).* Chips from the chipping machine shall be taken at regular intervals during the run being examined and immediately placed in a suitable, closed container. These portions shall be thoroughly mixed and sampled as under par. 3. Each final sample shall be of sufficient size to fill a one-gallon container, at least, and shall be packaged as under par. 4.4. Samples are not representative when water is used to lay the dust in chipping.

7.7 *Spent Materials.* A portion of material from the inner and outer areas of the top, middle and bottom of the leach shall be mixed for sampling, or 5 portions shall be taken from the pitch-hole as the spent material leaves the hole. The first portion shall be taken 5 minutes after starting to pitch and the last portion 5 minutes before pitching is completed. The intermediate portions shall be taken at equal time intervals between the fiirst and last portions. Each portion shall be of approximately equal size. Autoclaves should be sampled continuously from the spent material conveyor. These portions shall be thoroughly mixed and sampled as under par. 3. Each final sample shall be sufficient size to fill a one-gallon container, at least, and shall be packaged as under par. 4.4.

7.8 *Pasty Extracts.* Into each package selected for sampling, a sampling tool, as described under par. 6.4, shall be inserted to the middle of the package 3 times, side by side, and the samples so obtained emptied into a suitable container. If the sampling tool fails, a scoop or hatchet shall be used. All portions shall be cut into cubes of approximately one-half inch side and shall be thoroughly mixed and sampled as under par. 3. Each final sample shall be of sufficient size to fill a 2-quart Mason-type jar and shall be packaged as described under par. 4.3.

7.9 *Liquid Extracts.*

7.9.1 Samples of liquid extracts are not representative or official when they have been frozen, nor when steam has been passed directly into the extract. A suitable preservative shall be added to samples of liquid extract which are prone to ferment. All samples shall be sealed immediately to prevent loss of moisture.

7.9.2 *Liquid Extracts in Barrels.* The number of barrels to be sampled shall be determined from the table in par. 2.1 and shall be taken from evenly distributed parts of the total consignment. Before sampling, the contents of the selected barrels shall be mixed thoroughly by rolling. To assist in this mixing, two copper, or wooden, pailsful of the extract shall be withdrawn before rolling, the barrels rolled, the extract in the pails returned, and the barrels again rolled. Portions of at least one pound each shall be taken from each barrel through the bung-hole, avoiding contamination from the outside of the barrel. All such portions shall be of approximately equal size and collected in a suitable, covered container. The sample so obtained shall be thoroughly mixed and samples of at least 4 oz. taken and packaged as under par. 4.2.

7.9.3 *Liquid Extracts in Tank Cars* The extract shall be sampled as follows, while the tank car is being loaded or unloaded: A 1-quart portion shall be taken from the intake or discharge 3 minutes after the extract has begun to flow, and another 1-quart portion shall be taken at approximately 3 minutes before the flow ceases. Three other 1-quart portions shall be taken at equal time intervals between these two. These five portions shall be transferred to a suitable container as soon as taken, covered to prevent evaporation or contamination, thoroughly mixed, and samples of at least 4 oz. taken and packaged as under par. 4.2.

7.10 *Tannery Liquors.* The liquors shall be mixed by plunging, or other effective means, before sampling. If routine samples are taken daily for compositing, they shall be of equal size, and shall be mixed, and placed in covered containers. Samples of liquor for analysis shall be not less than 1 pint and shall be preserved with an anti-ferment. For this purpose, 0.5 g. of oil of mustard, oil of cloves, beta-naphthol (powdered) or p-nitrophenol per quart sample is recommended.

7.11 *Sampler's Certificate*

7.11.1 A sample drawn by an experienced sampler, adhering strictly to the methods of the Association, shall be considered Official. The following certificate shall accompany official samples:

> I (We), the undersigned sampler(s) of tanning material herein described:
>
> (see par. 7.11.2)

do affirm that the samples were taken in strict accordance with the Official Methods of the American Leather Chemists Association for the sampling of tanning materials.

Signed (sampler)

7.11.2 The description shall have the following data, whenever possible: Date sampled; kind of material; number of packages in the lot; distinguishing marks; number of packages sampled; weigher's lot number; any other marks descriptive of the lot sampled, such as car number, name of ship, order number, etc.

7.12 *Allowable Difference in Analysis.* The average of the tannin contents, found by the different laboratories on any sample taken by these methods of sampling, shall be calculated. For extracts, the allowable difference between laboratories shall be 1.5 per cent of this average tannin content: for raw materials, the allowable difference between laboratories shall be 3 per cent of this average tannin content. Where the actual tannin contents, found by any two laboratories, differ from each other by an amount greater than the allowable difference calculated above, the analysis shall be repeated by all parties concerned and, if this fails, the sampling shall be repeated, if possible, and new analyses run until agreement is reached.

A.L.C.A. Provisional Method February 1954

EXTRACTION OF RAW AND SPENT MATERIALS (A5)

1. SCOPE

1.1 This method is intended for use in extracting the tannin from raw and spent materials. The water extract, obtained by this method, is used for determining the total solids, soluble solids and soluble nontannins.

2. PREPARATION OF SAMPLE

2.1 All of the sample, drawn as directed under Method J10, shall first be ground in a rough grinder, or shredded, to pass a sieve having round openings one-half inch in diameter. After this grinding, the sample shall be mixed and quartered, as described under "Quartering of Samples" (Method J10), until about 1 lb. remains. This shall then be ground to pass a sieve having circular openings of 2 mm. diameter (U. S. Standard Sieve Series No. 10). This grinding shall be conducted in a Wiley mill or similar grinder.

2.2 Where the original sample is too wet to be ground, or where such grinding is likely to cause significant changes in the moisture content, samples of raw material shall be weighed, spread out on (canvas) trays which permit of a free circulation of air, and allowed to attain approximate equilibrium with the

laboratory atmosphere, the temperature at no time exceeding 60° C. Spent materials should be similarly treated except that temperatures up to 100°C. may be used. The partially dried sample shall then be ground as described in 2.1, above.

In all cases, the loss of moisture during such drying must be determined and the results of the analysis calculated to the basis of the original moisture before drying. A second moisture shall be run on the finely ground sample. The method of determining these moistures and calculating the original moisture is detailed under Method A6.

3. SPECIMEN

3.1 The specimen shall consist of a quantity of the sample, prepared as described in par. 2.1, sufficient to give as closely as possible 4 g. tannin per

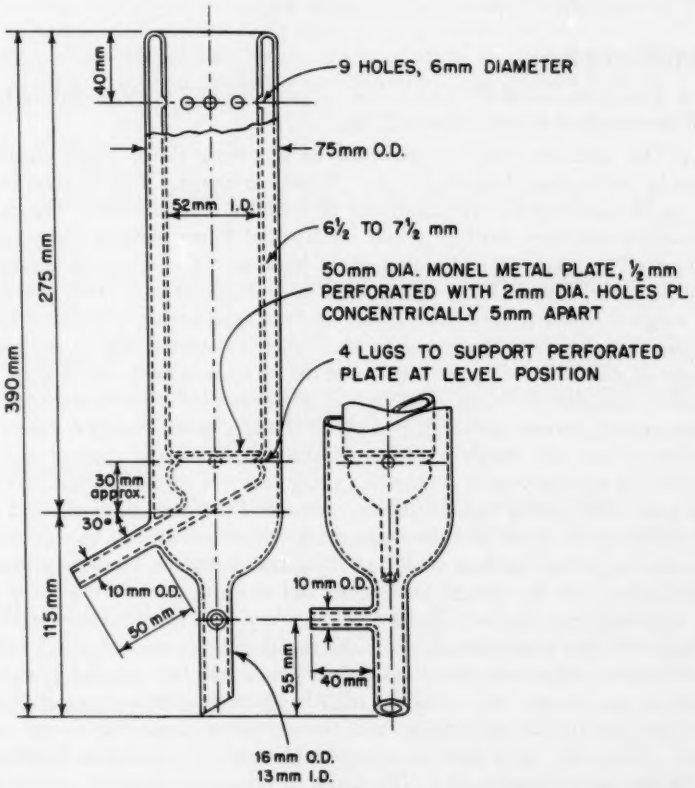


FIGURE A-5

liter of solution (not less than 3.75 g., nor more than 4.25 g., per liter). In the case of materials low in tannin, the specimen shall consist of the maximum quantity of the sample which can be extracted in the apparatus (see par. 5.6 and Method A22, par. 5.3).

4. APPARATUS AND REAGENTS

THE APPARATUS AND REAGENTS SHALL CONSIST OF THE FOLLOWING:

4.1 Steam-jacketed, Pyrex glass extraction apparatus as described in Figure A5.

4.2 Wiley mill, or similar grinder.

4.3 Formaldehyde: 40 per cent solution.

4.4 Toluene.

4.5 1-liter or 2-liter volumetric flasks. The M.C.A. type, with bulb in neck, is especially suitable for this type of work.

5. PROCEDURE

5.1 Raw materials shall be extracted to a volume of 2 liters; spent materials shall be extracted to a volume of 1 liter.

5.2 The extractor shall be attached to a boiling flask, which furnishes steam by the boiling of distilled water. A reflux condenser shall be attached to the top of the extractor and connected to a source of cold water. The outlet tube of the extractor shall be closed. A layer of Pyrex glass wool, 0.25 inch thick, shall be prepared and placed in the bottom of the extraction chamber, over the monel disc. The specimen shall be transferred to a tared container and weighed to the nearest 10 mg., taking every precaution to avoid changes in moisture content. The specimen shall then be wetted with a minimum amount of distilled water, at 95° C., and the mixture stirred with a glass rod to ensure complete wetting. The wetted specimen shall then be transferred, quantitatively, to the extractor, through a transfer funnel, using a minimum quantity of the hot distilled water. Entrapped air in the charge shall be removed by stirring with a glass rod, taking care not to disturb the layer of glass wool. The outlet tube of the extractor shall be opened slowly and the liquid allowed to drain into the appropriate receiving flask. At this stage, the water in the boiling-flask shall be boiling and the steam freely condensing in the jacket. As the charge settles, the rod and the sides of the extractor shall be rinsed with the hot, distilled water. Any solid material which comes through with the first extract, when the outlet tube is opened, shall be returned to the extraction chamber. When the water has drained from the surface of the charge, the specimen shall be covered with a layer of Pyrex glass wool about 0.25 inch thick, and the extractor connected to the condenser. The outlet tube shall be opened wide and the extraction continued for 7 hours at a uniform rate. To assist in obtaining uniform extraction,

it is recommended that the receiving flask be marked with 7 or more equal volume graduations, so that the rate of extraction can be easily gaged, and adjusted by regulating the generation of steam in the boiling-flask. The receiving flask shall be shaken every half hour, to mix the contents, and shall be protected from the heat of the burner during the extraction. The extraction shall be continued until the extract reaches the mark.

5.3 If the solution is likely to ferment (myrabolams or divi divi), 1 ml. of 40 per cent formaldehyde shall be added and the solution again mixed. In any event, the addition of from 3 to 4 drops of toluene is recommended to insure against mold growth during the overnight cooling.

5.4 Duplicate extracts shall be prepared.

5.5 The solution shall be cooled as directed in Method A12.

5.6 Where, as in par. 3.1, the tannin content of the material is so low that the maximum quantity of sample which can be extracted in the apparatus fails to give a solution containing 4.0±.25 g. of tannin per liter, the quantity of hide powder to be used in the determination of nontannins (Method A22, par. 4.3.1) shall be reduced proportionately. (See Method A22, par. 5.3).

A.L.C.A. Provisional Method February 1954

MOISTURE IN RAW AND SPENT MATERIALS (A6)

1. SCOPE

1.1 This method is intended for use in determining the moisture in raw and spent materials.

2. SPECIMEN

2.1 The specimen shall consist of approximately 10 g. of material from the sample prepared as described in Method A5, par. 2.

3. APPARATUS

3.1 Tannin dish (Method A20, par. 3.1) with suitable watchglass as cover.

3.2 Drying oven of circulating-air type, or Combined Evaporator and Dryer, specified in Method A13.

4. PROCEDURE

4.1 The specimen shall be transferred to a tared tannin dish and weighed to the nearest mg. The dish and specimen shall be placed in the oven and dried and cooled as specified in Method A13.

5. RESULTS

5.1 The amount of moisture in the specimen shall be calculated as follows:

$$\text{Moisture, per cent, } = \frac{W_2 - W_3 \times 100}{W_2 - W_1}$$

where: W_1 is the tare of the tannin dish
W_2 is the weight of dish plus specimen
W_3 is the weight of dish plus dry residue.

5.2 Two specimens from each sample shall be tested. The average of the results from the two specimens shall be taken as the moisture in the sample, except as described in 5.3, below:

5.3 When the original material was so wet that it had to receive a preliminary drying before being ground (Method A5, par. 2.2), the moisture content of the original material shall be determined as follows:

5.3.1 The whole of the original, wet, sample shall be weighed (W_1 g.). After having been dried, as described in Method A5, par. 2.2., the weight of the partially dried sample shall be determined (W_2 g.). Then:

$$\text{Loss of moisture in preliminary drying, per cent, } = \frac{W_1 - W_2 \times 100}{W_1} = \text{A per cent.}$$

5.3.2 The residual moisture (B per cent) in the partially dried and finely ground sample shall be determined as described in pars. 4 and 5, above.

5.3.3 Then the moisture in the original, wet sample shall be calculated as follows:

$$\text{Moisture in wet material, per cent, } = A + \left(B \times \frac{100 - A)}{100}\right)$$

5.4 The moisture shall be recorded to the nearest 0.01 per cent.

A.L.C.A. Provisional Method February 1954

PREPARATION OF SOLUTION OF LIQUID EXTRACTS (A10)

1. SCOPE

1.1 This method is intended for use in preparing a solution of liquid extract for use in the determination of the total solids, soluble solids and nontannins.

2. SPECIMEN

2.1 The specimen shall consist of an aliquot of the sample, prepared as described in Method J10, sufficient to give a solution containing as nearly as possible 4 g. of tannin per liter (not less than 3.75 g., nor more than 4.25 g., per liter).

3. APPARATUS AND REAGENTS

3.1 Formaldehyde: 40 per cent solution.

3.2 Toluene.

3.3 1-liter volumetric flask. The M.C.A. type, with bulb in neck, is especially suitable for this type of work.

4. PROCEDURE

4.1 Samples of liquid extracts, prepared as described in Method J10, shall be allowed to come to room temperature. The sample shall be thoroughly mixed at room temperature, and a specimen transferred to a tared container and stoppered to prevent loss of moisture. No material, which has been removed from the sample for any other purpose (e. g. for determination of specific gravity, etc.), shall be returned to the sample, and care must be taken that dried material around the neck of stopper of the sample bottle, does not contaminate the sample or specimen. The container and specimen shall be weighed to the nearest 0.1 mg.

4.2 Approximately 200 ml. of distilled water, at 95° C., shall be poured into a 1-liter flask and the specimen immediately transferred, quantitatively, into the flask with distilled water at 95° C. As soon as the specimen has been transferred, the contents of the flask shall be mixed by swirling. Sufficient distilled water, at 95° C., shall then be added to bring the volume to approximately 900 ml. and the solution shall again be mixed by swirling. The temperature of the solution, immediately after this mixing, shall not be less than 80° C.

4.3 If the solution is likely to ferment (myrabolams or divi-divi), 1 ml. of 40 per cent formaldehyde shall be added and the solution again mixed. In any event, the addition of from 3 to 4 drops of toluene is recommended to insure against mold growth during the overnight cooling.

4.4 Duplicate solutions, of 1 liter each, shall be prepared. It is permissible to prepare duplicate 2-liter solutions, in which case all appropriate volumes shall be doubled.

4.5 The solution shall be cooled as directed in Method A12.

A.L.C.A. Provisional Method February 1954

PREPARATION OF SOLUTION OF SOLID, PASTY AND POWDERED EXTRACTS (A11)

1. SCOPE

1.1 This method is intended for use in preparing a solution of solid, pasty, or powdered extract for use in the determination of the total solids, soluble solids and nontannins.

2. SPECIMEN

2.1 The specimen shall consist of a quantity of the sample, prepared as described in Method J10, sufficient to give a solution containing as nearly as possible 4 g. of tannin per liter (not less than 3.75 g., nor more than 4.25 g., per liter).

3. APPARATUS AND REAGENTS

THE APPARATUS AND REAGENTS SHALL CONSIST OF THE FOLLOWING:

3.1 Formaldehyde, 40 per cent solution.

3.2 Toluene.

3.3 Small mortar and pestle.

3.4 1-liter volumetric flask. The M.C.A. type, with bulb in neck, is especially suitable for this type of work.

4. PROCEDURE

4.1.1 The sample shall be emptied onto a sheet of clean, glazed paper, any large lumps roughly crushed, and the whole quickly mixed and quartered. From each quarter, a small portion (teaspoonful) shall be taken and shall be quickly crushed, transferred to a small, glass-stoppered weighing bottle, and be taken to the balance. Without delay, the analytical specimen shall be transferred to a tared container of suitable size and weighed to the nearest 0.1 mg. Each sample shall be handled individually, and all operations carried out as quickly as possible, up to this point, and all other precautions taken to minimize changes in moisture content.

4.1.2 *Pasty Extracts.* Where the extract has a moisture content such that it cannot be ground, the sample, broken or cut into small pieces, shall be weighed (W_1) and brought to approximate equilibrium with the laboratory atmosphere by drying for several hours at a temperature not exceeding 60° C., and then allowing to remain exposed to the air in the laboratory until the approximate equilibrium has been attained. The partially dried sample shall again be weighed (W_2). The original moisture content of the extract shall then be calculated as in Method A6, par. 5.3.3., except that the residual moisture in the air-dried material (B) shall be determined as in Method A20, par. 6.1, instead of as in Method A6, par. 5.3.2.

The air-dried sample, prepared as above, shall be treated as in par. 4.1.1., above. In such cases, the results of the analysis shall be calculated to the basis of the original moisture before drying.

4.2 Approximately 200 ml. of distilled water, at 95° C., shall be poured into a 1-liter flask and the container with the specimen placed in a funnel resting in the neck of the flask. Distilled water, at 95° C., shall be added to the extract, filling the container. The contents of the container shall then be stirred well and allowed to stand for a few moments so that any undissolved

particles may settle to the bottom of the container. The supernatant liquid shall then be decanted into the flask, more of the hot, distilled water added to the contents of the container, stirred and decanted, and the process shall be repeated until the soluble portion of the specimen has been completely dissolved and the whole of it washed into the flask. The contents of the flask shall then be mixed by swirling. Sufficient distilled water, at 95° C., shall then be added to bring the volume to approximately 900 ml. and the solution shall again be mixed by swirling. The full operation of dissolving and decanting, etc., shall be carried out as quickly as possible, and at no time during the operation shall the temperature of the solution fall below 80° C. If necessary, heat shall be applied to keep the solution above 80° C.

4.3 If the solution is likely to ferment (myrabolams or divi-divi), 1 ml. of 40 per cent formaldehyde shall be added and the solution again mixed. In any event, the addition of from 3 to 4 drops of toluene is recommended to insure against mold growth during the overnight cooling.

4.4 Duplicate solutions, of 1 liter each, shall be prepared. It is permissible to prepare duplicate 2-liter solutions, in which case all appropriate volumes shall be doubled.

4.5 The solution shall be cooled as directed in Method A12.

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COOLING OF ANALYTICAL SOLUTIONS (A12)

1. SCOPE

1.1 This method is intended for use in the cooling of the analytical solutions, prepared under Methods A10, A11 and A5, since the analytical results obtained are to some extent dependent on the conditions of cooling.

2. SPECIMEN

2.1 The specimen shall be the 1-liter or 2-liter solutions prepared as described above.

3. PROCEDURE

3.1 The prepared specimens shall be protected from drafts and shall be allowed to stand overnight in an ambient temperature of not less than 23° C., nor more than 28° C. When suitably protected, next morning the specimens will be found to be from 0° to 4° C. above room temperature. Just before proceeding with the analysis, the specimens shall be brought to 23° C. by immersing the flasks in water at not less than 22° C., swirling frequently to avoid local chilling. After their temperature has been adjusted, the solutions shall be made up to the mark with distilled water at 23° C. Where a constant-

temperature room is available, the specimens, suitably protected from drafts, may be cooled therein with advantage. In this case, the room shall be so controlled that solutions in flasks, exposed therein, shall remain at 24° C.

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EVAPORATION AND DRYING OF ANALYTICAL SOLUTIONS (A13)

1. SCOPE

1.1 This method is intended for use in evaporating and drying the 100 ml. portions of analytical solution, obtained in Methods A20, A21 and A22, so that consistent results may be obtained for the determination of total solids, soluble solids and nontannins in the sample. It is also intended for use in determining the moisture in the air-dry and prepared, wet, hide powders used in Method A22, and the moisture in Raw and Spent Materials (Method A6).

2. APPARATUS

All evaporation and drying of the above-mentioned specimens shall be conducted in either the Combined Evaporator and Dryer [*J.A.L.C.A.*, **9**, 442 (1914)], or the Precision-Freas Mechanical Convection oven [(*J.A.L.C.A.*, **45**, 669 (1950)], as directed below:

2.1 Combined Evaporator and Dryer. Where this apparatus is used:

A. the ventilation openings shall be unobstructed.

B. the temperature of the hot plate shall be within 1° C. of the boiling point of distilled water, at atmospheric pressure, at the location at which used (the tip of the thermometer shall dip into mercury held in a small flat-bottomed, metal cup placed on the hot plate.)

C. the steam chest shall be operated at atmospheric pressure.

2.2 Precision-Freas Mechanical Convection Oven. Where this apparatus is used:

A. it shall be operated at the temperature of boiling distilled water at the location at which used. Since the usual controls are sensitive to only ±0.5° C., they should be so adjusted that the average temperature is that of boiling distilled water, at atmospheric pressure, at the location at which used: that is, the temperature shall not fall more than 0.5° C. below, nor rise more than 0.5° C. above, that temperature.

B. the air-flow control-damper shall be one-quarter to one-half open.

C. the air intake and exhaust shall be opened 5 mm.

2.3 Desiccators and Desiccant.

2.3.1 The desiccators, used for cooling and desiccating tannin dishes and residues, shall be of glass and have an inside diameter of approximately 4 inches. The lids shall have knobs and wide, carefully ground, flanges and shall be interchangeable.

2.3.2 Only one tannin dish may be cooled in a desiccator at one time.

2.3.3 The desiccant shall be "Drierite", 8 mesh, either the indicating type, or the regular type into which at least one-fifth of its weight of the indicating type has been thoroughly incorporated. The desiccant shall be regenerated by heating to 200°–225° C. as soon as the blue of the indicator changes to pink.

3. PROCEDURE

3.1 The thermometers having been checked and the oven properly adjusted, as described in par. 2.1 or 2.2, the tared evaporating dishes, containing the aliquots of solution, or of hide powder, or of raw or spent tanning materials, to be dried, shall be placed in the oven and shall remain there for 17.0±1.0 hours.

3.2 When using the Precision-Freas oven (par. 2.2) , it is advisable that all heaters be in circuit.

3.3 At the end of the time, specified in par. 3.1, the dishes shall be removed, placed in desiccators, cooled to room temperature and weighed to the nearest 0.1 mg.

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TOTAL SOLIDS AND WATER (A20)

1. SCOPE

1.1 This method is intended for use in determining the total solids and water in extracts of vegetable tanning materials. The method is applicable to solutions of liquid, solid, pasty, and powdered extracts and to extracts of raw or spent materials.

2. SPECIMEN

2.1 The specimen shall consist of 100 ml. of a solution prepared as described in Methods A5, A10 or A11.

3. APPARATUS

THE APPARATUS SHALL CONSIST OF THE FOLLOWING:

3.1 Evaporating dish, Pyrex glass, 50 mm. tall, 70 mm. outside diameter, and weighing between 30 and 39 g. The bottom corner shall be rounded to a

radius of 6 mm., the bottom shall be flat and not cupped in the center, and the top edge rounded and polished.

3.2 100 ml. pipette: preferably with wide orifice and 15–20 seconds delivery time.

3.3 Drying oven or combined evaporator and dryer, as specified in Method A13.

4. PROCEDURE

4.1 The solution, prepared as described in Methods A5, A10 or A11, shall be thoroughly mixed by inverting and shaking 8-10 times, care being taken to ensure that all insoluble matter is uniformly dispersed and none left adhering to the walls of the flask. Immediately, a 150 ml. to 250 ml. portion (approximately) shall be poured into a bottle or other suitable container, stoppered or covered, and retained until the soluble solids and nontannins are ready to be pipetted. (See Method A1, par. 4.2.). Where the analysis is being performed in a constant-temperature room, however, the specimen may be pipetted from this portion at any convenient time. At the proper time, this secondary portion shall be thoroughly mixed by shaking, or stirring, so that the insoluble matter be uniformly distributed throughout the liquor and none remains adhering to the walls of the container. Immediately, the 100 ml. pipette shall be rinsed with the liquor, the rinsings being rejected. The liquor shall then be well stirred (to avoid air bubbles and the production of foam) and, while stirring, the tip of the rinsed pipette shall be immersed and the pipette filled, as quickly as possible, by suction. The level shall be brought to the mark as quickly as possible, and the 100 ml. specimen transferred into a tared evaporating dish. (Since tan liquors are very liable to foam and since they may contain large amounts of rapid-settling insoluble matter, the final mixing should be conducted so as to avoid foam formation, and the pipette should be filled and brought to the mark as quickly as possible.) The dish containing the specimen, together with the other dishes containing the specimens for soluble solids and nontannins (Methods A21 and A22), shall be placed in the drying oven and evaporated and dried as specified in Methods A13.

5. RESULTS

5.1 The amount of total solids in the sample shall be calculated as follows:

$$\text{Total Solids, per cent, } = \frac{(W_2 - W_1) \times 10}{W_3} \times 100$$

where:

W_1 is the tare of the evaporating dish

W_2 is the weight of dish plus dry residue

W_3 is the weight of specimen used in 1,000 ml. of the solution (Methods

A5, A10 or A11)

5.2 Since two specimens of each sample were taken in preparing the solutions (Methods A5, A10 or A11), two values for total solids will be obtained for each extract or tanning material. The average of these shall be taken as the percentage of total solids in the sample under test. (Duplicates are considered to be in good agreement when the per cent Total Solids differ by no more than 0.2.)

5.3 Record results to the nearest 0.01 per cent.

6. WATER

6.1 The amount of water in the sample shall be calculated as follows:

Water, per cent, = 100 minus per cent Total Solids

where:

per cent Total Solids is determined as in par. 5.1, above.

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SOLUBLE SOLIDS AND INSOLUBLES (A21)

1. SCOPE

1.1 This method is intended for use in determining the soluble solids and insolubles in extracts of vegetable tanning materials. The method is applicable to the analysis of liquid, solid, pasty, and powdered extracts and to extracts of raw or spent materials.

2. SPECIMEN

2.1 The specimen shall consist of 100 ml. of a solution prepared as described in Methods A5, A10 or A11, after being filtered as described hereunder.

3. APPARATUS AND REAGENTS

3.1 Evaporating dish. As Method A20, par. 3.1.

3.2 100 ml. pipette, preferably the same pipette as used in Method A20.

3.3 Filter paper: C.S. & S, No. 610, 21.5 cm. diameter, pleated so that it contains 32 evenly divided creases.

3.4 Cover glasses: approximately 150 mm. diameter.

3.5 Funnel: approximately 125 mm. diameter.

3.6 Kaolin. The kaolin used shall have been approved by a committee appointed by the Council of the A.L.C.A. and shall conform to the following specifications:

3.6.1 When 1.0 g. is suspended in 100 ml. of distilled water for 5 minutes, the suspension shall have a pH between 4.5 and 6.0. When 2.0 g. are shaken with 200 ml. of distilled water for 10 minutes and the mixture filtered, 100 ml. of the clear filtrate shall leave less than 0.001 g. of residue when evaporated and dried in a platinum dish.

3.7 Drying oven of circulating-air type, or Combined Evaporator and Dryer, as specified in Method A13.

4. PROCEDURE

4.1 A pleated filter paper shall be placed in a 125 mm. funnel. To 2.0 g. of kaolin in a clean glass container shall be added 25 ml. of the well-mixed analytical solution (prepared as described in Methods A5, A10 or A11) and the mixture stirred to a smooth paste. A further 200 ml. of the well mixed analytical solution (making 225 ml. in all) shall than be added and the mixture again stirred to a uniform suspension. Immediately, the suspension shall be poured onto the pleated paper in the funnel and the filtrate collected in the container in which the solution and kaolin were mixed. When about 40 ml. of the filtrate has been collected it shall be swirled, to pick up kaolin remaining in the container, and returned to the funnel. During this and subsequent operations, funnels and containers shall be kept covered to avoid changes due to evaporation, and the temperature of the solution and of the filtrates shall be maintained between 23° and 25° C. The operation of collecting and repouring 40 ml. of filtrate shall be repeated as many times as is necessary until the solution has been in contact with the filter paper for exactly one hour. At the end of the hour, the solution shall be syphoned out of the filter as completely as possible, taking care not to disturb the kaolin film on the paper. This liquid shall be discarded. Immediately, the paper shall be refilled with 225 ml. of the well-mixed analytical solution which has been kept at a temperature of 23°–25° C. The kaolin film shall be disturbed as little as possible during this operation and best results are obtained by carefully pouring the solution into the center of the cone. No solution additional to this 225 ml. shall be poured onto the filter paper. When 40 ml. of the filtrate have passed through, the next portion shall be collected in a clean, dry, glass container and, when about 125 ml. have been collected, the container shall be removed from beneath the funnel. This 125 ml. shall be checked for clarity by swirling and viewing against the light. If not clear it shall be rejected, and the determination rerun using a new filter. If the filtrate is clear, it shall be mixed with a clean rod and the 100 ml. specimen pipetted into a tared evaporating dish (see Method A1, par. 4.2). The pipette should be that used for transferring the specimen used for determining total solids (Method A20) and shall be rinsed with a portion of the filtrate before measuring the specimen. The dish containing the specimen, together with the other dishes containing the specimens for total solids and nontannins, shall

be placed in the drying oven and evaporated and dried as specified in Method A13.

5. RESULTS

5.1 The amount of soluble solids in the sample shall be calculated as follows:

$$\text{Soluble Solids, per cent, } = \frac{(W_2 - W_1) \times 10}{W_3} \times 100$$

where:

W_1 is the tare of the evaporating dish

W_2 is the weight of dish plus dry residue

W_3 is the weight of specimen used in 1,000 ml. of the solution (Methods A5, A10 or A11).

5.2 Since two specimens of each sample were taken in preparing the solutions (Methods A5, A10 or A11), two values for soluble solids will be obtained for each extract or tanning material. The average of these shall be taken as the percentage of soluble solids in the sample under test. (Duplicates are considered to be in good agreement when the per cent Soluble Solids differ by no more than 0.2)

5.3 Record results to the nearest 0.01 per cent.

6. INSOLUBLES

6.1 The amount of Insolubles in the sample shall be calculated as follows:
Insolubles, per cent, = per cent Total Solids minus per cent Soluble Solids

where:

per cent Total Solids is determined as in Method A20, and
per cent Soluble Solids is determined as in par. 5.1, above.

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NONTANNINS AND TANNIN (A22)

1. SCOPE

1.1 This method is intended for use in determining the soluble non-tannins and tannin in extracts of vegetable tanning materials. The method is applicable to the analysis of liquid, solid, powdered and pasty extracts and to extracts of raw and spent materials.

2. SPECIMEN

2.1 The specimen shall consist of 100 ml. of a solution prepared as described in Methods A5, A10 or A11, after being detannized and filtered as described hereunder.

3. APPARATUS AND REAGENTS

3.1 Evaporating dish. As Method A20, par. 3.1.

3.2 Drying oven of circulating air type, or Combined Evaporator and Dryer, as specified in Method A13.

3.3 Filter paper; C. S & S, No. 610, 21.5 cm. diameter. It shall be pleated so that it contains 32 evenly divided creases.

3.4 Cover glasses; approximately 150 mm. diameter.

3.5 Volumetric flasks; graduated *to deliver* 200 ml. (Nontannin Flask).

3.6 Funnels; approximately 125 mm. diameter.

3.7 Shake bottles; 32-ounce, with rubber stoppers. The bottles shall be approximately 8.5 inches overall height and 3.5 inches diameter.

3.8 Shaking machine of the rotating type, equipped to hold 32-ounee bottles for end over end agitation of hide powder and analysis solution. The speed of rotation shall be 60 ± 2 r.p.m., and the machine shall be so constructed that the side of the shakebottle adjacent to the rotating shaft shall be not less than 2 inches nor more than 3 inches from the center of the shaft.

3.9 Cloth. The cloth shall be of cotton, with a nominal (unbleached) thread count of 48 x 48 and a weight of 1.65 yards per pound. When bleached, the thread count will be approximately 52–53 x 43–48. (Suitable cloths are: "Indianhead, Bleached, Preshrunk, Permanent Finish", from Textron, Inc., 1407 Broadway, New York 18; and "Ramona", from J. C. Penney Co., 330 West 34th St., New York 1.)

3.10 Perforated filter discs of porcelain, plastic, or other material impermeable to, and unaffected by, the analytical solutions; the perforations being no larger than 3 mm. diameter.

3.11 Kaolin. The kaolin shall be as specified in Method A21, par. 3.6 and 3.6.1.

3.12 Chrome Alum Solution. This shall be a 3 per cent solution, prepared by dissolving $CrK(SO_4)_2 \cdot 12H_2O$ in distilled water at room temperature (3 g. per 100 ml. of solution). The solution shall not be more than 30 days old when used.

3.13 Hide Powder. The hide powder shall have an ash content of less than 0.3 per cent and shall have an acidity such that, when 7.0 g. of air-dry powder are suspended in 100 ml. of 0.1 *N* KCl and the mixture set aside for 24 hours

with occasional shaking, the pH of the filtrate shall be not less than 5.0, nor more than 5.4. It shall show a water soluble content not exceeding 0.004 g. when carried through the procedure for the determination of nontannins (par. 4.3.2-4), using distilled water instead of the analytical solution. It shall give an average nontannin percentage which shall differ by less than ±0.2 from the comparable nontannin percentage obtained with the next preceding official hide powder when the two hide powders are tested simultaneously against certain standard extracts.

3.13.1 However, no hide powder shall be official except it has been approved by a committee appointed by the Council of the A.L.C.A., which committee shall consist of 5 members and be appointed for one year, but shall continue to serve until its successor committee has been appointed. The Hide Powder Committee shall have the right to approve or disapprove any hide powder, regardless of whether the hide powder meets the specifications above, and its decision shall be final. All hide powder shall cease to be official at the end of 3 years from the date on which it was declared official by the committee.

3.13.2 Hide powder, prepared as described in par. 4.2, shall be used for the analysis of tanning materials (par. 4.3.1) on the same day that it is prepared.

3.14 100 ml. pipette; preferably the same pipette as used in Method A20, 3.2.

4. PROCEDURE

4.1 Five grams of the air-dry hide powder shall be transferred to a tared glass dish (par. 3.1) and weighed to the nearest milligram. The dish and powder shall be placed in the drying oven (Method A13) for a period of 17.0±1.0 hours. The dish and dried contents shall be cooled in a desiccator to room temperature and the percentage of moisture calculated.

4.2 The amount of oven-dry hide powder required will equal 12.5 g. times the number of specimens to be analyzed, plus 12.5 g. times 2 (for blanks), plus 5.5 g. (for determination of moisture in the wet powder). That is, 12.5 g. x (n + 2) + 5.5 g. of oven-dry powder.

Such an amount of air-dry hide powder as is equivalent to the weight of oven-dry powder calculated above, plus 10-15 g. of air-dry powder to allow for mechanical loss, shall be digested with 10 times its weight of distilled water at 23° C. to 25° C. for 30 minutes, being stirred three or four times during this period. Then 1.0 ml. of the 3 per cent chrome alum solution shall be added for each gram of the air-dry powder taken, and the whole mixed well. The mixture shall be stirred or mixed every 15 minutes for 2 hours and then allowed to stand, covered, overnight at a temperature of not less than 23° C. nor greater than 28° C. Next morning, the mixture shall be poured into a large piece of cloth (par. 3.9), the excess liquid allowed

to drain off, and the powder squeezed or pressed to approximately 75 per cent moisture. The cake shall be broken up and washed by digesting with 4 successive portions of distilled water at 23°-25° C., each portion equal in amount to 15 times the weight of air-dry powder taken. The hide powder shall be well suspended in the water each time, all lumps being broken up, and each digestion shall last for 15 minutes. The hide powder shall be squeezed or pressed to approximately 75 per cent moisture after each digestion, except the last. The wet hide powder used for the analysis shall contain as nearly as possible 72.5 per cent moisture (not less than 71 per cent nor more than 74 per cent.

4.3 While the hide powder is being washed, each 200 ml. volumetric (nontannin) flask shall be filled to the mark with its appropriate, well-mixed analytical solution. Two of the 200 ml. flasks shall also be filled to the mark with distilled water, as blanks. These aliquots shall be maintained at 23°–25° C.

4.3.1 Without delay, after washing, a quantity of wet hide powder (72.5 ±1.5 per cent moisture), equivalent to 12.5 ± 0.3 g. of oven-dry hide powder, shall be weighed out and transferred to each of the shake bottles, and the bottles immediately closed with rubber stoppers. 20 g. of the wet powder shall also be weighed out into a tared dish for the determination of moisture in the prepared hide powder.

4.3.2 Without delay thereafter, the 200 ml. aliquots and blanks, previously measured out, and at a temperature of 23°–25° C., shall be added to the hide powder in the respective shake bottles and the flasks allowed to drain for not less than 15 seconds nor more than 30 seconds. The flasks shall then be removed, the bottles stoppered and placed in the shaking machine and shaken for exactly 10 minutes. At the end of this time, they shall be removed and the contents emptied onto a cloth (par. 3.9) or perforated plate (par. 3.10) held in a 125 mm. funnel, the filtrate being collected in a suitable glass container containing 2 g. of kaolin. The drained powder shall be lightly squeezed so that the volume of filtrate is approximately 135 ml. The total time of contact between the hide powder and the tannin solution shall be not less than 13 minutes nor more than 15 minutes, from the time the solution first comes in contact with the hide powder until it is squeezed therefrom.

4.3.3 The filtrate and kaolin shall be thoroughly mixed, and then be filtered through an official paper into the original container in which they were mixed. The filtrate shall be returned to the filter until it becomes clear, when a clean container shall be substituted and the clear filtrate finally collected. During these and subsequent operations, funnels and containers shall be kept covered to avoid changes due to evaporation, and the temperature of the solution and filtrates shall be maintained at 23°–25° C. Normally, the filtrate must be returned three to five times before true clarity can be

assured. The final filtrate shall be tested for clarity by swirling and viewing against the light, and, if clear, the 100 ml. specimen pipetted into a tared evaporating dish (see Method A1, par. 4.2). The pipette should be that used for transferring the specimens for total and soluble solids (Methods A20 and A21) and shall be rinsed with a portion of the filtrate before measuring the specimen. The dish containing the specimen, together with the other dishes containing the specimens for total and soluble solids, shall be placed in the drying oven and evaporated and dried as specified in Method A13.

5. RESULTS

5.1 The percentage of non-tannins in the specimen shall be calculated as follows:

$$\text{Nontannins, per cent, } = \frac{F \times (W_2 - W_1) \times 10}{W_3} \times 100$$

where: W_1 is the tare of the evaporating dish
W_2 is the weight of the dish plus dry residue
W_3 is the weight of the specimen used to prepare 1 liter of the solution (Methods A5, A10, A11)

$$F = \frac{200 + (\text{grams of water in wet hide powder added to solution in 4.3.2})}{200}$$

5.2 The residue from the blanks (W_2 - W_1) shall not exceed 0.004 g., as specified under par. 3.15.

5.3 Where, as in Method A5, par. 5.6, it has been necessary to reduce the quantity of prepared hide powder used in the detannization, the formula in par. 5.1 applies, provided the factor (F) be correctly calculated for the lesser quantity of water introduced in par. 4.3.1.

5.4 Since two specimens of each sample were taken in preparing the solutions (Methods A5, A10, or A11), two values for nontannin will be obtained for each extract or tanning material. The average of these shall be taken as the percentage of nontannin in the sample under test. (Duplicates are considered to be in good agreement when the per cent nontannins differ by no more than 0.2)

6. TANNIN

6.1 The amount of tannin in the sample shall be calculated as follows:

Tannin, per cent, =per cent Soluble Solids minus per cent Nontannins

where: per cent Soluble Solids is determined as in Method A21, par. 5.1, and
per cent Nontannins is determined as in 5.1, above.

(Duplicates are considered to be in good agreement when the duplicate values for Tannin differ by no more than 0.3.)

6.2 The average of these duplicate values for tannin shall be taken as the percentage of tannin in the sample under test.

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ANALYSIS OF TANNERY LIQUORS (A25)

1. SCOPE

1.1 This method is intended for the analysis of tannery liquors made up from vegetable tanning materials.

2. SAMPLES AND SPECIMENS

2.1 The sample shall be taken as under Method J10, par. 7.10.

2.2 The specimen shall be of such size that, when diluted with distilled water, the analytical solution shall contain as nearly as possible 7.0 g. total solids per liter, except where such dilution would give over 3.5 g. tannin per liter. In such case, the specimen shall be of such size that, when diluted with water, the analytical solution shall contain as nearly as possible, but not exceed, 3.5 g. tannin per liter, irrespective of solids content.

3. DILUTION

3.1 Where the liquor is of 65° Bk., or over, the specimen shall be diluted with water at 40° C., and cooled as under Method A12.

3.2 Where the liquor is less than 65° Bk., the specimen shall be diluted with water at 23° C.

4. PROCEDURE

4.1 Total Solids shall be determined as in Method A20.

4.2 Soluble Solids and Insolubles shall be determined as in Method A21.

4.3.1 Nontannins and Tannin shall be determined as in Method A22, except that the quantity of hide powder used (Method A22, par. 4.3.1) shall be adjusted according to the following table:

Tannin grams per liter	Dry Hide Powder grams per 200 ml.
3.50	9.1
3.00	7.8
2.50	6.5
2.00	5.2
1.50	3.9
1.00	2.6

4.3.2 In calculating the actual nontannin, the factor F in the formula of Method A22, par. 5.1, must be calculated according to the weight of water contained in the actual amount of hide powder used for each specimen.

5. TOTAL ACIDITY OF LIQUORS

5.1 *Apparatus and Reagents*: Method I.

5.1.1 One percent gelatin solution, neutral to brom-cresol purple. The addition of 25 ml. of 95 per cent ethyl alcohol per liter is recommended to prevent frothing. The solution shall be adjusted to neutrality to brom-cresol purple with 0.1 *N* acetic acid or 0.1 *N* sodium hydroxide.

5.1.2 Kaolin; as specified in Method A21, par. 3.6 and 3.6.1.

5.1.3 0.1 *N* Sodium hydroxide solution.

5.2 *Apparatus and Reagents*: Method II.

5.2.1 Pipette: 6 ml.

5.2.2 pH Meter: glass/calomel electrodes.

5.2.3 0.1 *N* Sodium hydroxide solution.

5.3 *Procedure*

5.3.1 Method I. To 25 ml. of sample in a cylinder which can be stoppered shall be added 50 ml. of the gelatin solution and the mixture diluted to 250 ml. with distilled water. 15 g. of kaolin shall then be added and the mixture shaken vigorously. The mixture shall then be allowed to settle for at least 15 minutes. A 30 ml. aliquot of the supernatant solution shall then be withdrawn, diluted with 50 ml. of distilled water, and titrated with 0.1 *N* sodium hydroxide, using brom-cresol purple as indicator.

5.3.2 Method II. A 6 ml. aliquot of the sample, transferred to a suitable titration vessel (100 ml. capacity) of an electrometric titration apparatus, shall be diluted with 75 ml. of distilled water and titrated with 0.1 *N* sodium hydroxide to pH = 6.0.

5.4 *Results*

5.4.1 Method I. 1 ml. 0.1 *N* sodium hydroxide is equivalent to 0.2 per cent acetic acid.

5.4.2 Method II. 1 ml. 0.1 *N* sodium hydroxide is equivalent to 0.1 per cent acetic acid.

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SUGAR IN TANNING MATERIALS (A30)

1. SCOPE

1.1 This method is intended for use in determining the sugars present in tanning materials.

2. APPARATUS AND REAGENTS

2.1 Saturated normal lead acetate solution.
2.2 Dipotassium hydrogen phosphate, anhydrous (K_2HPO_4).
2.3 Toluene.
2.4 Fehlings Solutions, A and B.
2.5 Concentrated HCl (sp. gr. 1.18).
2.6 Kerosene.
2.7 Saturated solution of sodium hydroxide.
2.8 Phenolphthalein solution.
2.9 Filter paper; C. S & S, No. 610, 21.5 cm diameter.

3. PROCEDURE

3.1 To 400 ml. of a solution of tanning material, of analytical concentration (4.0 ± 0.25 g. tannin per liter), shall be added 50 ml. of a saturated solution of normal lead acetate. The mixture shall be well shaken and allowed to stand for from 5 to 10 minutes. The mixture shall then be filtered through a folded filter paper, the filtrate being returned until it is clear. From 360 to 380 ml. of the clear filtrate shall be collected, usually requiring that the filter be drained for an hour or more. The volume of collected filtrate shall be measured in a cylinder and the excess lead removed therefrom with dried di-potassium hydrogen phosphate (K_2HPO_4), using 2.5 g. of the phosphate per 100 ml. of the filtrate and weighing the phosphate to 0.1 g. After the phosphate has been added, the mixture shall be well shaken for 4 or 5 minutes and shall then be filtered through a folded filter paper.

3.2 *Reducing Sugars.* To 100 ml. of the clarified, de-leaded, solution, obtained in par. 3.1, shall be added 33.3 ml. of distilled water and, if the reduction is not to be made at once, also from 8 to 10 drops of toluene, the mixture being well shaken and stoppered with a plug of cotton. The prepared solution shall be kept in a cool place and the reduction made within the following 24 hours. When ready for reduction, the solution shall be filtered if toluene has been added. Reducing sugars shall be determined by the Munson and Walker procedure (Method B10), using duplicate, 50 ml. aliquots.

3.3.1 *Total Sugars.* To 150 ml. of the clarified, de-leaded, solution, obtained in par. 3.1, in a 500 ml. Erlenmeyer flask, shall be added 7.5 ml. of concentrated hydrochloric acid, and the mixture boiled under a reflux condenser for exactly 1 hour. (If the solution foams at the start, which is unusual, from 5 to 10 drops of kerosene shall be added.) The flask shall then be removed, loosely stoppered when moderately cool, and allowed to stand until ready for reduction, usually overnight. The solution shall then be cooled in ice-water for from 20 to 30 minutes, 2 drops of phenolphthalein added, carefully neutralized with the saturated solution of sodium hydroxide, and then concentrated hydrochloric acid added, drop by drop, until the color of the in-

dicator is just discharged. After being brought to laboratory temperature, the solution shall be transferred to a 200 ml. volumetric flask, made to the mark with distilled water, mixed, and filtered until clear. Total sugars shall be determined by the Munson and Walker procedure (Method B10), using duplicate, 50 ml. aliquots.

3.3.2 Where the solution of tanning material contains appreciable amounts of magnesium salts, the hydrolysis shall be carried out as in par. 3.3.1. The solution shall then be cooled in ice water for from 20 to 30 minutes, 2 drops of phenolphthalein added, neutralized with the saturated solution of NaOH and 2 drops be added in excess. Without delay, the mixture shall be transferred to a 200 ml. volumetric flask, diluted to volume with distilled water, mixed, and filtered clear. During the filtration, the filtrate shall be kept just acid by the addition, from time to time, of small portions of powdered, pure tartaric acid. Total sugars shall be determined, immediately, by the Munson and Walker procedure (Method B10), using duplicate, 50 ml. aliquots.

4. RESULTS

4.1 *Reducing Sugars.* After the weight of the cuprous oxide has been corrected for the blank of the Fehling's solution, the equivalent milligrams of dextrose shall be found from Munson and Walker's table (Method B10). To express as per cent dextrose, the milligrams of dextrose shall be multiplied by 3 and divided by the grams of sample per liter of solution.

4.2 *Total Sugars.* Shall be calculated as directed under "Reducing Sugars", par. 4.1.

4.3 *Non-Reducing Sugars.* The percentage of non-reducing sugars shall be calculated by subtracting the percentage of reducing sugars (par. 4.1) from the percentage of total sugars (par. 4.2).

A.L.C.A. Provisional Method February 1954

COLOR TESTS WITH SHEEPSKIN SKIVER (A40)

1. SCOPE

1.1 This method is intended for use in making color tests of all types of vegetable tanning extracts and of extracts of vegetable tanning materials.

2. SPECIMEN

2.1 The specimen shall consist of a liquor of 4 times analytical strength, prepared in a manner similar to the preparation of solutions for analysis (Methods A5, A10, A11), and the volume shall be 400 ml. for Method I (par. 5.2) or 250 ml. for Method II (par. 5.3).

3. APPARATUS AND REAGENTS

3.1 Pickled sheepskin skiver: specially selected for color test.

3.2 Borax.

3.3 Suitable, resistant containers: 10-liter capacity, and 3- to 4-liter capacity.

3.4 Acetic acid: glacial.

3.5 Sodium acetate: crystal.

3.6 Sodium chloride.

3.7 Shake bottles (32 oz.).

3.8 Flat dish (photographic tray): capacity 250 ml. to 300 ml.

3.9 Rubber, photograph print-roller.

4. PREPARATION OF SKIVER

4.1 The neck and flank portions of the skiver shall be trimmed off, leaving a skin of uniform grain. The skiver may now be cut into pieces approximately 4 inches by 6 inches, or may be left whole. The skiver shall be placed in a solution of 50 g. of borax dissolved in 8 liters of distilled water and at a temperature of 23° - 25°C. It shall be stirred, or agitated, frequently and, at the end of 4 hours, be transferred to a fresh borax solution, made up as before, be stirred several times and then allowed to remain overnight therein at not less 23° C nor more than 28° C. Next morning, the skiver shall be transferred to 8 liters of a 0.1 per cent solution of acetic acid, at 23° - 25° C, be stirred, or agitated, frequently and, at the end of 3 hours, be placed in a fresh solution of acetic acid of the same volume, strength and temperature, and be stirred, or agitated, frequently. At the end of 3 hours, the skiver shall be placed in 2 liters of an acetic acid—sodium acetate buffer solution, at 23° - 25° C, containing 2.0 g. glacial acetic acid and 10 g. of sodium acetate crystals per liter, and having a pH of 4.8 to 5.0. The skiver shall be stirred therein several times and then allowed to remain therein overnight. Next morning, the skiver shall be transferred to a saturated solution of sodium chloride containing a large excess of the salt.

5. MAKING COLOR TESTS

5.1 The salt shall be removed from the skiver sample (4 inches by 6 inches) by shaking with 4 changes of distilled water, of 500 ml. each and at 23° - 25° C, in a shake bottle for about 15 minutes each.

5.2 *Method I*—Shake Method. The skiver sample shall be added to the 400 ml. specimen (par. 2.1) at 23° - 25° C, contained in a shake bottle. Immediately, the bottle shall be stoppered and be shaken for 1 hour in the shake machine (Method A22, par. 3.8). The skiver shall be allowed to stand in the

solution overnight at 23° - 28° C. and then be shaken for one-half hour next morning. The skiver shall then be treated as described in par. 5.4, below.

5.3 *Method II*—Layaway Method. From the 250 ml. specimen (par. 2.1), 50 ml. shall be taken, diluted to 200 ml. with distilled water at 23° - 25° C., and be poured into a flat dish or tray. The skiver sample (4 inches by 6 inches) shall be completely immersed in this solution, grain side up, and be rocked occasionally for 1 hour, or until the skiver is evenly colored. The weak solution shall then be discarded. Immediately, the remaining 200 ml. of the specimen shall be poured into the dish and the skiver be completely immersed therein. It shall be rocked occasionally, be covered to prevent dust or dirt from falling onto the skiver, and be allowed to stand overnight at 23° - 28° C. The skiver shall then be treated as described in par. 5.4, below.

5.4 The skiver, tanned as described in pars. 5.2 or 5.3, above, shall be washed by shaking with two changes of distilled water, of 800 ml. each and at 30° - 35° C, for 10 minutes each, and shall be rinsed with distilled water, and squeezed out a number of times before, between, and after the changes of water. It shall then be spread out on a glass surface and be slicked out lightly, using a rubber, photograph print-roller, just enough to remove excess water. The skiver shall then be tacked out, grain side down, on a board covered with filter paper, and shall be put into a dark place to dry.

A.L.C.A. Provisional Method February 1954

LIGNOSULFONATES (SULFITE CELLULOSE) (A50)

1. SCOPE

1.1 This method is intended for use in detecting the presence of lignosulfonates (sulfite cellulose) in extracts of tanning materials.

2. APPARATUS AND REAGENTS

2.1 Aniline.

2.2 Concentrated hydrochloric acid.

2.3 Comparison solution: this shall contain lignosulfonate (sulfite cellulose) in the proportion of one part total solids to 2,000 ml. of solution, and as much tanning material, similar to that being tested but known to be free from lignosulfonate, as will make up the solution to analytical strength.

3. SAMPLE AND SPECIMEN

3.1 The sample shall be drawn as under Method J10.

3.2 The specimen shall consist of five ml. of a solution of analytical strength (4.0 g. tannin per liter), prepared as described in Methods A5, A10, A11.

4. PROCEDURE

4.1 The specimen shall be placed in a test tube, 0.5 ml. of aniline added, and the whole well shaken. 2 ml. of concentrated HCl shall then be added, and the mixture be again well shaken.

5. RESULTS

5.1 If at least as much precipitate remains at the end of 15 minutes as is obtained when the comparison solution is similarly treated, the material shall be held to contain lignosulfonates (sulfite cellulose) and the fact shall be noted on the analysis report.

5.2 Attention is drawn to the fact that some synthetic tannins give precipitates under the conditions of this method.

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OFFICIAL CERTIFICATION (A60)

1. On public analytical work by members of this Association, the fact that the Official Method has been used shall be stated on the report.

2. OFFICIAL FORM FOR THE REPORTING OF ANALYSES OF EXTRACTS

Report of Analysis

	Per Cent		*Per Cent*
Tannin.....		Total Solids.....	
Nontannins.....		Soluble Solids.....	
Insolubles.....		Specific Gravity.....	
Total	100.00		

Ratio of Tannin to { Total Solids..... Per Cent
Soluble Solids..... Per Cent

Analyzed according to the methods of the A.L.C.A.

3. OFFICIAL FORM FOR THE REPORTING OF ANALYSES OF RAW AND SPENT TANNING MATERIALS

Report of Analysis

Extractives	*Per Cent*
Tannin.....	
Nontannins.....	

Insolubles.....
Non-Extractives.....
Water.....

Total 100.00

Total Extractives.....
Soluble Extractives.....

Ratio of Tannin to { Total Extractives..... Per Cent
Soluble Extractives..... Per Cent

Analyzed according to the methods of the A.L.C.A.

A.L.C.A. Provisional Method February 1954

The Preservation of Hides with Used Salt

By C. C. KRITZINGER and J. H. M. VAN ZYL

INTRODUCTION

South African salt is produced by the solar system in open pans and is therefore subject to all the varied changes in climatic conditions. During the rainy season there is always a normal decrease in the production, but under adverse conditions of excessive rains or drought it often happens that hide and skin curers find much difficulty in obtaining sufficient salt supplies. They are then forced to re-use salt to tide their plants over such difficult times.

Such re-use of salt has always been condemned for three reasons. In the first place it is argued that used salt contains large numbers of putrefactive bacteria which have become adjusced to living in high concentrations of salt. Whilst this is undoubtedly true, it is also true that any possible bacterial decay arising from used salt can be overcome completely through the application of sodium silicofluoride. In the second place re-use of salt results in the occurrence of more salt stains. Finally, it is maintained that used salt penetrates less readily and therefore does not dehydrate the hide rapidly enough. Although the literature abounds with vague statements to this effect, there is very little evidence that such is actually the case, hence the following experiments were conducted.

EXPERIMENTAL PROCEDURE

Six pieces of hide, measuring about 6″x6″, were cut from the butt of a heavy hide on opposite sides of the backbone line, washed and fleshed. The

experiment was done in duplicate, salting two corresponding samples with the same salt, and using 50% salt on green weight.

Three grades of salt were used. Sample No. 1 was pure unused salt, while samples 2 and 3 were from used batches which had been mixed with other salt. The salt was spread on the floor for a few days to become dry to more or less the same degree. All the samples were sifted through a 6 mesh sieve (2.8 mm.) and the larger crystals discarded. About 100 grams of each sample were kept in stoppered bottles for analysis.

The test hide pieces were inserted between wet-salted hides which had been in stack for a few days, to simulate practical curing conditions, as described in an earlier paper [11].

A sample strip was cut from each square after 0, 1, 2, 4, 6, 12, 22 and 36 hours curing. The strips were cut longitudinally to the backbone, starting nearest the bellies and then cut into ¼ inch cubes for analysis. Analyses for moisture, sodium chloride and hide substance were carried out by methods described earlier [11].

Table I shows the analysis of the three samples of salt used in this work, all values except moisture and iron being expressed on a moisture-free basis.

TABLE I

Analysis of Curing Salt

Salt	H_2O	% Cl	$\%SO_4$	% Ca	% Mg	Total Fe ppm	% Total insoluble mat.	% Comb. Matter
1	0.08	59.9	1.76	——	0.17	50	0.10	trace
2	0.36	58.3	2.76	0.17	0.28	100	1.39	0.93
3	0.74	58.0	1.96	0.09	0.20	120	2.88	2.06

The most significant difference between the three salts is the increase in the insoluble matter, corresponding to an increase in the combustible matter. In all other respects all three samples would pass the specifications suggested by Kritzinger [7] and since accepted by the South African Bureau of Standards. Sample No. 3 has perhaps a slightly high iron content, the maximum allowed being 100 parts per million. The specifications require the salt to show less than 0.5% insoluble matter.

Table II shows the influence of salt purity upon the rate of penetration of the sodium chloride and the rate of dehydration of the hide. The values for sodium chloride shown are those depicting the concentration of sodium chloride in the residual moisture of the hide, and in the same manner the moisture content of the stock has been expressed as a percentage on the hide substance.

TABLE II

The Influence of Salt Purity upon Salt Penetration and Dehydration

(a) % NaCl on Moisture

Salt sample	HOURS 0	1	2	4	6	12	22	36
1	0.93	7.7	10.1	13.4	17.5	27.6	30.2	31.5
2	1.10	7.3	10.1	13.6	16.7	26.6	31.2	32.7
3	0.85	7.0	9.9	14.0	18.2	26.5	28.7	32.5
				(b) % H_2O on Hide Substance				
1	194	164	150	132	121	105	101	104
2	194	163	152	131	124	105	101	101
3	194	161	152	133	123	106	101	107

These results, shown graphically in Fig. 1, leave little doubt that within the limits of the experimental procedure and the range of salt purity there is no difference in the rate of penetration or the rate of dehydration, i. e. the rate or efficiency of curing, between the three samples of salt.

It was deemed advisable to check these findings, when using salt of even less purity. Three further samples of salt were therefore obtained and used in the same manner described above.

TABLE III

Analysis of Curing Salt

Salt	H_2O	% Cl	% SO_4	% Ca	% Mg	Total Fe. ppm	% Total insoluble mat.	% Comb. matter
1	1.10	58.6	1.08	0.11	0.44	85	1.41	0.76
2	0.35	58.7	1.40	0.09	0.23	120	1.74	1.16
3	1.86	58.4	1.53	0.09	0.28	210	3.94	2.85

It will be seen that none of these samples would pass the Bureau of Standards Specification for insoluble matter or magnesium, and that only Sample 1 conforms with the specification for total iron. The insoluble matter was largely composed of organic materials, probably mostly blood. Such blood would also account for the high iron content of Samples 2 and 3. Sample 3 was taken from a batch of salt which had been re-used four times on hides without adding clean salt at any stage, and was in exceptionally bad condition. It is believed that even under the worst curing conditions such dirty salt would never be found in use.

The hide pieces were analyzed as before and the results given in Table IV, and depicted in Figure 2.

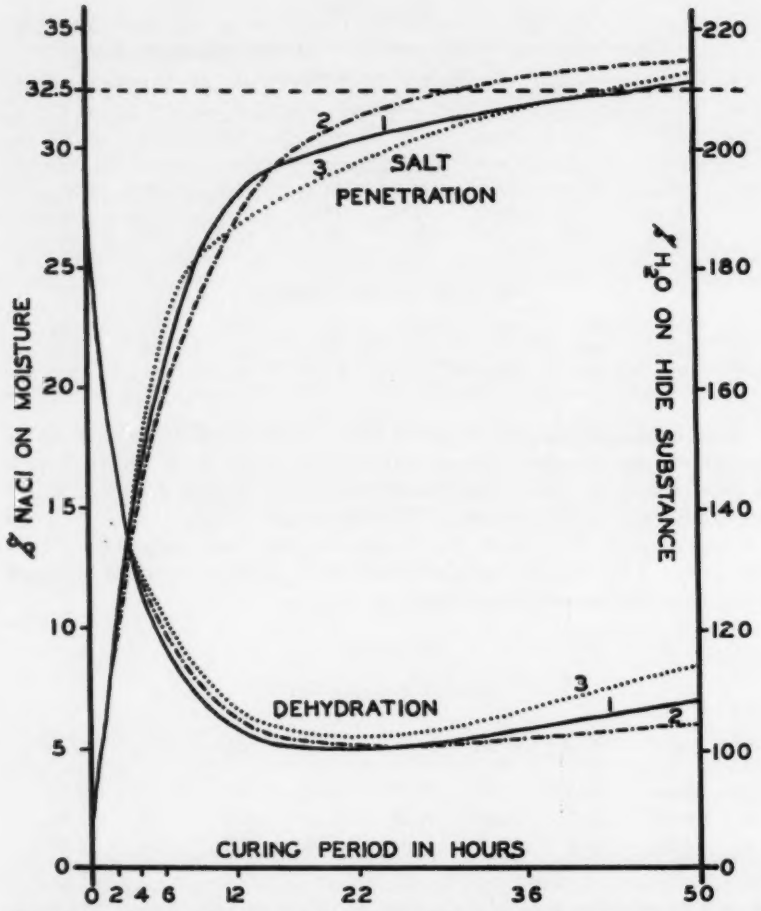

FIGURE 1.—The Influence of Salt Purity upon Salt Penetration and Dehydration. (% NaCl on moisture and % H_2O on hide substance.

Again therefore no difference can be detected between the three samples of salt used in this experiment or between these samples and the previous set.

Discussion of the Results

The literature on the curing of hides and skins abounds with statements regarding the deleterious effects of re-using salt, but a diligent search failed to reveal sufficient experimental evidence for many of the claims. This applies

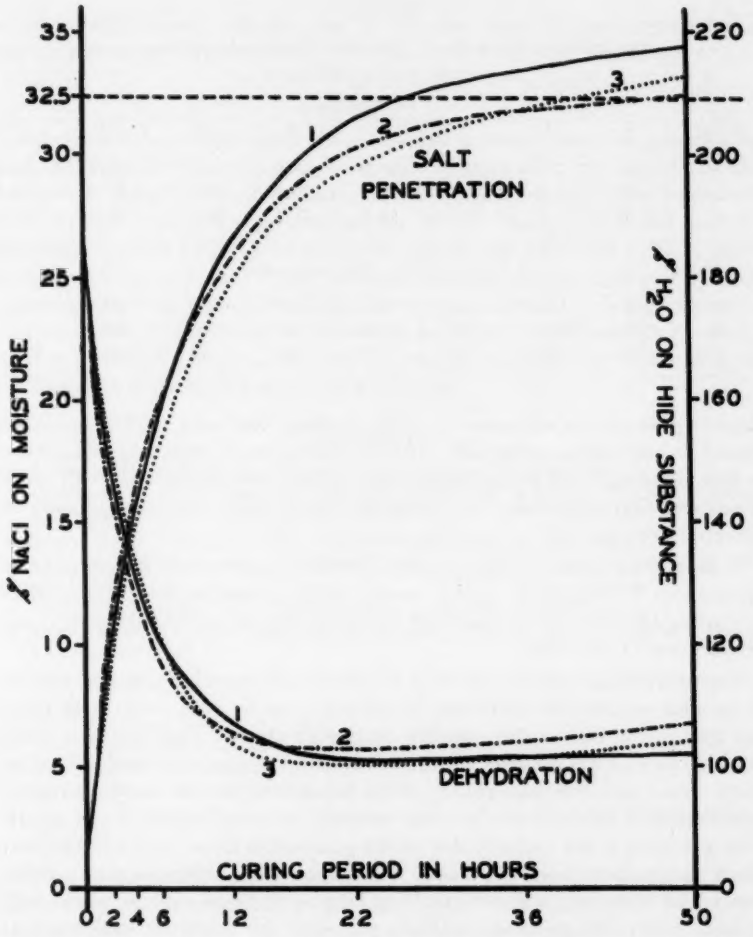

FIGURE 2.—The Influence of Salt Purity upon Salt Penetration and Dehydration. (Second Series) (% NaCl on moisture and % H_2O on hide substance).

more specifically to the question of the influence of insoluble impurities upon the rate of salt penetration and the rate of dehydration of the hide.

McLaughlin, Blank and Rockwell [10] state that used salt crystals are coated with impurities arising from previous use, and that the rate of absorption must therefore be slower. A similar attitude is taken by Frey [4] and Jordan Lloyd [6]. Hevesi [5] states that sand and stones will damage the hide grain and

TABLE IV

The Influence of Salt Purity upon Salt Penetration and Dehydration

(a) % NaCl on Moisture

Salt sample	HOURS 0	1	2	4	6	12	22	36
1	0.85	7.4	10.7	15.0	18.6	27.5	30.5	34.0
2	0.93	7.3	10.7	15.1	19.3	27.0	30.3	32.9
3	0.91	7.1	10.2	14.0	17.5	26.9	29.5	32.7
				(b) % H_2O on Hide Substance				
1	201	161	152	133	122	107	101	102
2	192	162	151	130	119	107	102	103
3	197	162	150	133	124	104	101	103

Bravo[8] goes to the extreme of recommending that only 0.05% insolubles should be allowed in curing salt. The attitude of most writers on this subject is that dirty salt will retard penetration of the sodium chloride, will result in stock of dirty appearance and will lead to more stains and more pronounced bacterial attack.

It is obvious from the experiments described above that the presence of up to about 4% insoluble matter, most of which is combustible, cannot effect the curing efficiency of the salt with regard to the rate of salt absorption and dehydration of the hide.

The other disadvantages of used salt have not been discussed in the experimental section but there can be no doubt as to their validity as there has been in the case of the question dealt with above. Used salt is inclined to yield stock of less pleasing appearance, but the appearance need not necessarily reflect upon the true quality of the hides or skins. Secondly, it is quite true that used salt will result in the presence of more stains on the goods. This is mostly, if not entirely, due to the presence of larger quantities of iron which accumulates from the blood. Kritzinger[7a] has shown experimentally that stains from iron will not result as long as the iron content of the salt remains below 100 parts per million, provided the hides are well washed. Furthermore, he has shown that iron stains are more likely to develop in hides not treated with a bactericide such as sodium silicofluoride, due to the action of bacteria upon the iron and other impurities.

The third factor for consideration is the presence in used salt of large numbers of putrefactive bacteria which have already become accustomed to living in high concentrations of sodium chloride[1, 3, 4, 10]. Such bacteria will attack the hide substance quite rapidly and readily and their presence in used salt is perhaps the biggest factor militating against re-use. However, this advantage can be completely overcome by the treatment of the hides

or skins with sodium silicofluoride in solution form, or preferably in this respect by mixing not less than 2% of this chemical with the salt [8], [9].

Summary

Experimental evidence has been presented proving that the presence of up to 4% insoluble matter in used hide salt will not affect the rate of salt absorption or dehydration of the hide, and that therefore salt may be re-used on hides provided certain precautions are taken. These precautions include, first and foremost the treatment of the hides or the salt with sodium silicofluoride to overcome the adverse effects of the presence in used salt of large numbers of salt-resistant putrefactive bacteria. Secondly, it is recommended that used salt should never be reused as such but should always be mixed with at least fifty per cent. new salt in order to maintain the iron and other impurities content at as low a level as possible.

References

1. Anderson, H., *J. Intern. Soc. Leather Trades' Chemists*, **29**, 215 (1945).
2. Bergmann, M. and Hausam, W., *Ledertechn. Rdsch.*, **24**, 26 (1932). Through *J. Intern. Soc. Leather Trades' Chemists*, **16**, 33 (1933).
3. Bravo, G. A., Through *J. Am. Leather Chemists Assoc.*, **29**, 588 (1934).
4. Frey, R. W., *The Leather Manufacturer*, **12**, 309 (1932). Through *Collegium*, **755**, 178 (1933).
5. Hevesi, A., Through *J. Am. Leather Chemists Assoc.*, **32**, 604 (1937).
6. Jordan Lloyd, D., The Preparation of Empire Hides and Skins. Imperial Institute, London, 1937.

7a Kritzinger, C. C., *Leather Ind. Res. Inst. Res. Bull.* No. 8, 1945. Grahamstown, South Africa.

7. ——, *ibid*, No. 9, 1945.
8. ——, *J. Am. Leather Chemists Assoc.*, **45**, 203 (1950).
9. ——, *ibid*, **46**, 445 (1951).
10. McLaughlin, G. D., et al, *ibid*, **23**, 300 (1928).
11. van Zyl, J. H. M., *Leather Ind. Res. Inst. Res. Bull.* No. 108, 1951. Grahamstown, South Africa.

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Studies on the Flow of Brine from Wet-Salted Hides

By C. C. Kritzinger and J. H. M. van Zyl

When solid salt is applied to the surface of fresh hide some of that salt will dissolve in the surface moisture to form a brine which is more concentrated than the salts solution inside the hide, consequently the forces of osmosis

and diffusion are set in motion in an attempt to equalize the concentration inside and outside the hide. Equilibrium is reached when all the residual moisture is saturated with salt. This process proceeds to a greater extent towards the outside, as witnessed by the flow of brine away from a stack of wet-salted hides, and may continue to a slight extent even after equilibrium in the salt concentrations has been set up, saturated brine leaving the hides due to pressure and other factors. Such brine also brings with it a certain amount of brine-soluble protein material.

The present study has been designed to obtain information on various factors which affect the rate of brine-flow and the removal of nitrogen from the hide, since this flow of brine is of practical importance insofar as it largely determines the degree of shrinkage from the green to the cured condition.

Experimental Procedue

In each of the experiments to be described below a fresh hide was split along the backbone line and the halves then treated as required. From each half about 20 pounds was cut in squares of about 8″ x 8″, the two lots being weighed accurately. Sampling was started along the backbone and finished towards the bellies until the required weight was obtained, using mostly butt and shoulder areas. These two lots of pieces were salted separately hair to flesh in two containers constructed in such a way that the brine could run freely to the bottom where a channel led into a measuring cylinder. Inside the containers were fitted wire gauze cages to prevent the brine from washing solid salt into the cylinders and to keep all the salt on the samples which fitted tightly into the cages. The cages were supported away from the sides of the containers so that nothing would impede the flow of brine. The bottom of the cages was of perforated wood. By this means evaporation could be kept to a minimum. A stack of this type could be built within ten to fifteen minutes, using about 50% good quality salt on green weight.

The brine was collected in quantities of about 200 ml., measuring the exact weight and volume of each aliquot and recording the time. For the first aliquot the time was taken from the moment the first piece of hide received its salt. Collection was discontinued when no further flow could be observed, usually after about five to seven days under these conditions of salting. In each aliquot collected the nitrogen and sodium chloride were determined by conventional methods[14]. In two typical runs the variation in the sodium chlorides concentration was as shown in Table I.

It will be observed that even the first aliquot has very nearly reached the maximum concentration and that variation is limited. Even after 144 hours the concentration remains only slightly above 31% and, in the calculations below, this average figure was therefore taken.

TABLE I

The Concentration of NaCl (Weight on Volume %) in Brine Flowing from Wet-Salted Hides

Time Hrs.	Min.	% NaCl	Time Hrs.	Min.	% NaCl
1	30	30.7	1	26	30.5
2	33	30.8	2	26	30.75
3	46	30.8	3	33	30.85
5	03	30.95	4	45	30.95
6	35	30.95	6	08	30.95
8	15	30.85	7	36	30.85
10	21	30.95	9	19	31.15
12	31	31.05	11	03	31.15
14	52	31.15	13	09	31.05

Nitrogen values shown in the Tables record the percentage of the total hide nitrogen present in each aliquot collected as well as the total percentage removed at the end of each stage.

In each experiment the following weights were recorded in addition to those which appear in the Tables:

1. The green weight of the hide pieces,
2. The weight of salt applied,
3. The cured weight of the pieces after brushing off all the excess salt crystals,
4. The wet and dry weight of the salt and equipment left after curing.

From these weights could be calculated as a percentage on the hide green weight the shrinkage, moisture retained by the salt, moisture lost by evaporation and salt taken up by the hide pieces. From the brine was determined the total amount of water collected.

I. The Influence of Washing

In the first experiment one half of the hide was left in the bloody condition whilst the other was well washed and drained for about 30 minutes before sampling. 2% sodium silicofluoride was mixed with the salt before application to the pieces.

The results are recorded in Tables II, III and IV and shown in Fig. 1 and 2.

Brine flow started from the washed samples ten minutes after the first piece had been salted, and in the unwashed samples after seventeen minutes. The first drop appearing in the measuring cylinder was taken as the start of flow.

TABLE II

Brine Collected from Washed and Unwashed Wet-Salted Hides

(Green weight of washed samples 8,830 grams, unwashed samples 8,850 grams)

Treatment:		Washed				Unwashed				
Time Hrs.	Min.	Volume ml.	Weight gm.	% on green weight	% of Total	Time Hrs.	Min.	Volume ml.	Weight gm.	% on green weight	% of Total
	34	201	242	2.73	6.23	1	14	202	242	2.74	6.78
1	03	401	483	5.43	12.4	1	57	402	484	5.44	13.5
1	33	601	724	8.12	18.6	2	42	604	727	8.18	20.3
2	06	803	967	10.1	24.8	3	36	805	969	11.0	27.1
2	50	1005	1210	13.7	31.1	4	37	1005	1210	13.7	33.8
3	35	1205	1451	16.4	37.3	5	47	1207	1453	16.4	40.7
4	32	1407	1693	19.1	43.6	7	09	1410	1698	19.2	47.5
5	33	1609	1935	21.8	49.7	8	36	1616	1946	22.0	54.4
6	51	1809	2176	24.6	56.0	10	26	1820	2192	24.7	61.3
8	14	2009	2417	27.2	62.2	12	31	2024	2438	27.5	68.2
9	56	2209	2658	29.9	68.4	15	19	2226	2681	30.2	75.9
12	01	2409	2899	32.6	74.5	19	19	2425	2921	32.9	81.6
14	48	2612	3144	35.4	80.7	25	29	2631	3169	35.7	88.6
18	53	2810	3383	38.0	86.9	36	54	2839	3420	38.5	95.5
26	10	3008	3622	40.8	93.0	148	34	2969	3577	40.3	100.0
55	28	3204	3858	43.3	99.0						
148	03	3237	3898	43.8	100.0						

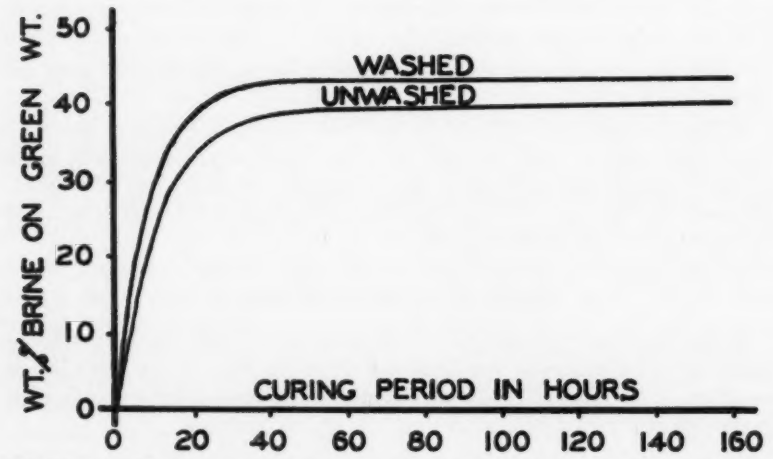

FIGURE 1.—The Influence of Washing upon the Flow of Brine From Wet-Salted Hides.

It will be seen from Table II and Fig. 1 that the washed sample yielded more brine and at a faster rate than the unwashed pieces. Fifty per cent of the total brine collected during the seven days flowed off during the first

5½ hours in the washed sample, but in the unwashed set this mark was reached only after 7½ hours. At the end of curing (seven days) the washed pieces had yielded 43.8% of their green weight in weight of brine, whilst the unwashed had yielded only 40.3%, so that it is clear that more water has run off the washed pieces. On the other hand, the washed pieces had contained more water initially, as will be shown later. Hausam [2, 4] obtained results somewhat lower than those recorded here, probably due to the fact that he used unwashed hides and skins and cured his stock in a practical manner where more evaporation could take place and less water could flow from the stacks.

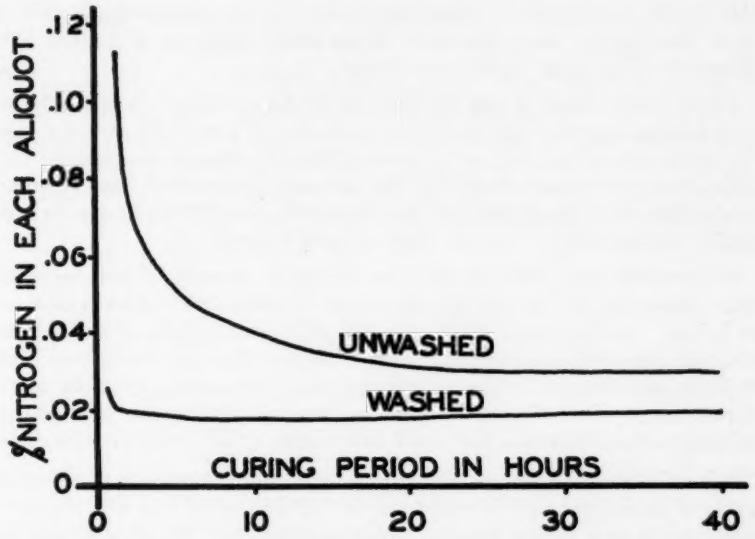

FIGURE 2.—The Effect of Washing upon the Nitrogen Present in Brine Flowing from Wet-Salted Hides.

TABLE III

Shrinkage and Water Loss in Hides Cured for Seven Days (With and Without Previous Washing)

(All percentages calculated on green weight)

	Washed	Unwashed
% Shrinkage	24.7	21.0
% Salt absorbed by hide	12.9	12.7
% Water collected	32.4	29.7
% Water retained by excess salt	2.5	1.3
% Water evaporated	2.7	2.7
% Total water lost by hides	37.6	33.7

At a first glance it would appear that the washed hides yielded less cured stock than the unwashed. But the former had absorbed slightly more salt than the latter, and since the residual moisture inside the hide merely becomes saturated and not super-saturated with salt, it follows that the washed hides had retained more water after curing than the unwashed. The difference in shrinkage figures, brine and water loss is thereofre due to water taken up during washing, but a small proportion of this water appears to be left behind in the hides, so that the actual yield will be slightly higher.

It is interesting to note that 2.7% of the total water loss of 37.6% (respectively 33.7%) is due to evaporation even despite the precautions taken in this work. Furthermore, taking the figures for the unwashed pieces it is clear that slightly more than half of the initial moisture of a green hide (normally 65%) is lost during wet-salting.

Finally, from Table II and Fig. I it will be observed that whilst the difference between the two lots in the total amount of brine collected was only 4% at the end of say 144 hours, it was about 6% after ten hours of curing. This means that water flow from the unwashed pieces had been retarded by the presence of blood and dirt, thus confirming on a different basis the conclusion reached earlier [14] on the effect of foreign matter.

McLaughlin and Theis [9] found that a certain amount of hide proteins could be washed out by soaking fresh corium of hides and calfskins in saturated brines. Stather and Herfeld [10] stated that these soluble proteins were albumine, globuline and mucine. They [11] showed that the concentration of the brine has a definite influence upon the rate of extraction, obtaining maximum removal with 2% sodium chloride solutions. Kritzinger [6] studied the full range of concentration and found best results at 10% sodium chloride.

It is quite reasonable to expect some variation in the amount of nitrogen extracted during the early hours of wet-salting, due to the fact that the concentration of such soluble proteins varies from one layer to the next [7] and to the fact that the concentration of the brine as it enters the hide will go through all phases until saturation is reached inside the hide. It will, however, be difficult to show these variations in the nitrogen concentration of the brine since it will be concealed by the presence of blood proteins which are extracted rapidly during the first few hours of curing. Stather and Herfeld [13] determined the nitrogen in the brine obtained from different curing procedures, but unfortunately gave no results for one procedure which was comparable to the one used in the present work. Hausam [3] confirmed this work and also tabulated results [4] obtained from the brine analysis of twenty stack-salted calfskins cured with 44% salt on weight. The brine samples were taken at different stages of the curing process. The results, with regard to the nitrogen content, are quite high compared to those shown in Table IV below. High results could be expected from his work since calfskins contain more soluble

protein material and since the skins were apparently salted down without washing.

In Table IV has been recorded the information on nitrogen extracted from the pieces in the present work. The nitrogen in each aliquot is calculated as a percentage of the total hide nitrogen present in the pieces and the total nitrogen removed at the end of each stage is shown. These values have been plotted in Fig. 2 which shows only the nitrogen present in each aliquot collected.

TABLE IV

The Effect of Washing upon the Nitrogen present in Brine Flowing from Wet-Salted Hides

Treatment:		Washed				Unwashed	
Time Hrs.	Min.	% N in each aliquot	% Total nitrogen	Time Hrs.	Min.	% N in each aliquot	% Total nitrogen
	34	.0260	.026	1	14	.1130	.113
1	03	.0200	.046	1	57	.0753	.188
1	33	.0197	.066	2	42	.0654	.254
2	06	.0195	.085	3	36	.0591	.313
2	50	.0192	.104	4	37	.0539	.367
3	35	.0187	.123	5	47	.0494	.416
4	32	.0185	.142	7	09	.0457	.462
5	33	.0179	.160	8	36	.0439	.506
6	51	.0176	.177	10	26	.0394	.545
8	14	.0173	.194	12	31	.0362	.581
9	56	.0176	.212	15	19	.0346	.616
12	01	.0175	.230	19	19	.0317	.648
14	48	.0178	.247	25	29	.0309	.679
18	53	.0182	.266	36	54	.0304	.709
26	10	.0194	.285	148	34	.0218	.731
55	28	.0223	.307				
148	03	.0346	.342				

From these results it will be seen that the presence of blood leads to the presence of much larger quantities of nitrogen in the brine, most of the blood being removed from the pieces during the first few hours[4], although even after 36 hours there is still blood present in the brine. In the washed pieces some blood will seep from the blood vessels in the hide during the first few hours, hence the rapid fall in the nitrogen content of the brine. After about fifteen hours the nitrogen again rises slightly, probably as a result of breakdown of the proteins by the salt and sodium silicofluoride. In the unwashed pieces the presence of large quantities of blood even at this stage masks such a possible increase. The removal of such nitrogen is a desirable feature of curing and should not be viewed with alarm, unless the nitrogen loss is due to bacterial action.

II. The Influence of Stack Pressure

In the first experiment the miniature stacks were only about 20 pieces high. The second experiment was therefore planned to vary the pressure in the stack. The hide was cut up as before, but here the entire hide was given a wash beforehand. Sodium silicofluoride was again mixed with the salt. One stack was built as before, and the second, after completion, was weighted down with sufficient weight to give a pressure on the bottom hide piece corresponding to a stack-height of about 100 hides in normal procedure.

In Table V are shown the results on the brine collected over a period of seven days, these results having been plotted in Figure 3. From the results it is obvious that pressure on the stack of hides has resulted in the loss of more brine from the pieces, the difference being 5.5% for the two stacks. This greater loss of brine takes place during the first 1½ hours, after which the rate of brine flow for the two stacks remains about the same. This means that whereas brine is left on the hides in the small stack, it is pressed out of the other very quickly so that the hides do not get the opportunity of reabsorbing some of that brine. It is probable that only brine between hides is pressed out and not brine from inside the hide itself. The inference of these results is that the higher the stack the more would be the shrinkage, at least

TABLE V

The Effect of Pressure upon Brine Flow from Wet-Salted Hides

(Green weight of sample with pressure 9,000 grams, without 9,120 grams)

Treatment:	Without Pressure				With Pressure				
Time Hrs. Min.	Volume ml.	Weight gm.	% on green weight	% of Total	Time Hrs. Min.	Volume ml.	Weight gm.	% on green weight	% of Total
47	198	238	2.61	6.20	24	198	238	2.65	5.33
1 22	401	482	5.28	12.1	54	399	480	5.34	11.15
1 54	599	720	7.89	18.7	1 14	601	723	8.93	16.75
2 26	802	964	10.53	25.0	1 34	799	961	10.67	22.15
3 04	1003	1206	13.2	31.3	1 57	997	1199	13.3	27.8
3 49	1205	1449	15.9	37.6	2 28	1197	1440	16.0	33.45
4 42	1405	1690	18.5	43.8	3 03	1401	1686	18.7	39.1
5 42	1606	1932	21.2	50.0	3 45	1601	1927	21.4	44.7
6 47	1808	2175	23.9	56.4	4 35	1803	2170	24.1	50.4
8 09	2011	2419	26.5	62.6	5 34	2006	2414	26.8	56.0
9 49	2213	2662	29.2	69.0	6 43	2208	2657	29.5	61.6
11 49	2415	2905	31.9	75.4	8 01	2411	2901	32.3	67.4
14 42	2621	3153	34.5	81.7	9 43	2613	3144	34.9	73.0
20 52	2829	3403	37.3	88.2	11 58	2817	3390	37.7	78.7
33 52	3029	3644	40.0	94.4	15 08	3015	3628	40.3	84.3
142 52	3209	3861	42.4	100.0	20 38	3218	3872	43.0	89.7
					33 38	3422	4118	45.7	95.4
					142 38	3582	4311	47.9	100.0

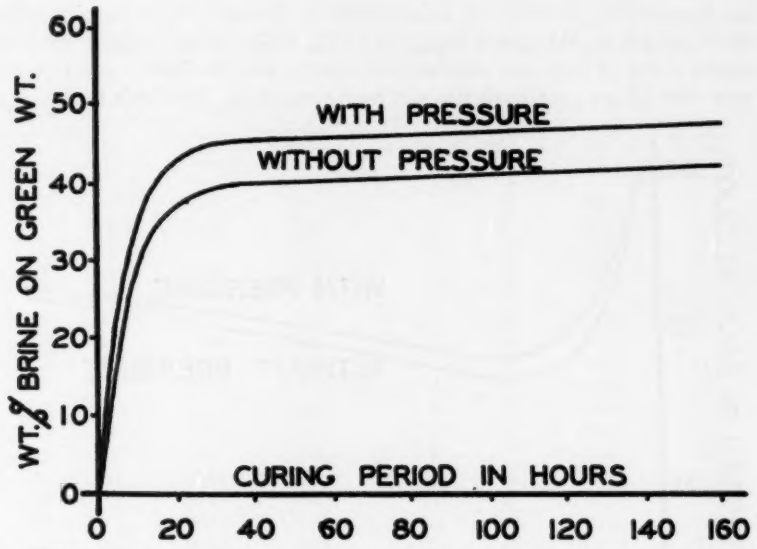

FIGURE 3.—The Influence of Pressure upon the Flow of Brine from Wet-Salted Hides.

under the condition of experimentation. Table VI also shows that the shrinkage is only 23.7% for the small stack and 30.0% for the stack with pressure. It must be borne in mind, however, that the pieces used in this work were quite small and the salt of small crystal size, hence brine could run off much easier than in normal practice. It is clear, nevertheless, that further work on full scale is required on this question.

Hausam [2] obtained a shrinkage figure of 8% in a stack of twenty hides. This figure is very low compared to results in normal practice, where shrink-

TABLE VI

Shrinkage and Water Loss in Hides Cured for Seven Days (With and Without Extra Stack Pressure Applied)

(All percentages calculated on green weight)

	Normal pressure	Extra pressure
% Shrinkage	23.7	30.0
% Salt absorbed by pieces	12.2	10.5
% Water collected	31.2	35.2
% Water retained by salt	0.7	0.6
% Water evaporated	3.8	4.7
% Total water lost by hides	35.7	40.5

age figures of up to 20% are quite common. Hausam found an absorption figure for salt on hide green weight of 19.2% which is much higher than the results reported here and obtained by Stather and Herfeld[12], and it would seem that all the excess salt had not been removed in Hausam's work.

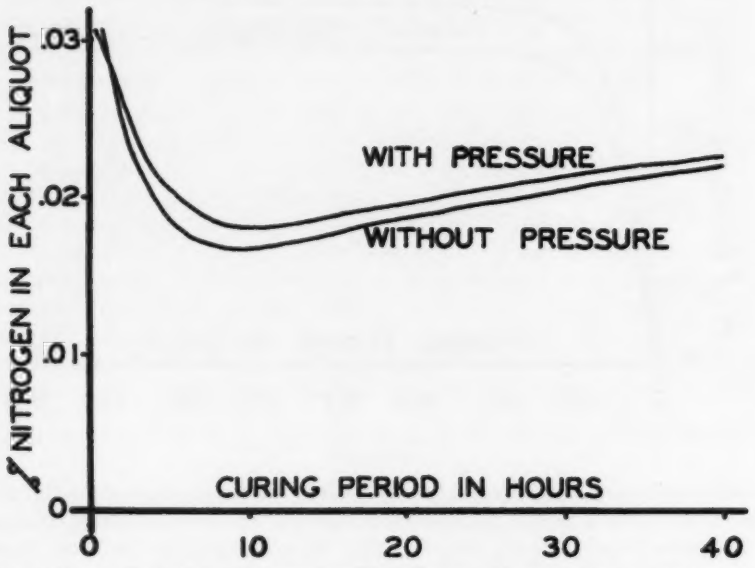

FIGURE 4.—The Effect of Pressure upon the Nitrogen Present in Brine Flowing from Wet-Salted Hides.

Table VI shows that the total water loss in the stack with extra pressure is about 5% higher than in the normal stack, but at the same time the hides had taken up less salt than in the normal. This is due to the fact that the brine is pressed out from between the pieces before the hide has time to reabsorb it. The shrinkage in the normal stack is slightly lower than in the previous experiment (washed hides) and the total water loss is also somewhat lower. This is due to better drainage after washing. Finally, it is interesting to note that the evaporation loss is higher than previously, as a result, no doubt, of the drier atmosphere which prevailed.

It will be observed that the pieces which had been under more pressure yielded more total nitrogen than the corresponding group and to a certain extent this must be ascribed to the fact that the former pieces yielded more brine, hence would bring out more nitrogen. On the other hand it will be noted that the concentration of nitrogen in comparable aliquots was always higher for the pressed pieces. Pressure seems to have caused more blood

TABLE VII

The Effect of Stack Pressure upon the Nitrogen Present in Brine Flowing Wet-Salted Hides

Treatment:		Normal pressure				Extra pressure	
Time Hrs.	Min.	% N in each aliquot	% Total nitrogen	Time Hrs.	Min.	% N in each aliquot	% Total nitrogen
	47	.0305	.031		24	.0305	.031
1	22	.0272	.058		54	.0296	.061
1	54	.0244	.082	1	14	.0283	.089
2	26	.0235	.106	1	34	.0266	.116
3	04	.0223	.128	1	57	.0257	.142
3	49	.0208	.149	2	28	.0246	.166
4	42	.0190	.168	3	03	.0238	.190
5	42	.0180	.186	3	45	.0216	.212
6	47	.0176	.203	4	35	.0206	.232
8	09	.0171	.220	5	34	.0200	.252
9	49	.0168	.237	6	43	.0193	.272
11	49	.0171	.254	8	01	.0185	.290
14	42	.0181	.272	9	43	.0183	.308
20	52	.0191	.292	11	58	.0181	.327
33	52	.0215	.313	15	08	.0186	.345
142	52	.0255	.339	20	38	.0203	.365
				33	38	.0221	.388
				142	38	.0235	.411

to be squeezed out of the pieces, as could also be observed in the colour of the brine. See Figure 4.

It will again be seen that there is a slight rise in the concentration of nitrogen removed towards the end of the curing period, as observed in the first experiment.

III. The Influence of Sodium Silicofluoride

In the third experiment the hide was washed and sampled as before, but here one set of pieces was salted with salt containing 2% sodium silicofluoride. The results are recorded in Table VIII and depicted in Figure 5 to show the flow of brine.

It is clear that the presence of sodium silicofluoride in the salt results in less brine running off the hides and at a slower rate, right from the beginning of the cure. At the end of three days the silicofluoride hides show 3.7% less brine loss (weight on green hide weight) than the control pieces.

This relationship is also shown in Table IX where the shrinkage figures are given. It will be observed that the shrinkage for the silicofluoride pieces is only 19.9% as against 23.3% for the control pieces. From the silicofluoride pieces a total of 2.7% less water could be accounted for in the weights.

TABLE VIII

The Effect of Sodium Silicofluoride upon Brine Flow from Wet-Salted Hides
(Green weight of sample without silicofluoride 9,180 grams, with 9,460 grams).

Treatment:		Without Silicofluoride				With Silicofluoride					
Time Hrs.	Min.	Volume ml.	Weight gm.	% on green weight	% of Total	Time Hrs.	Min.	Volume ml.	Weight gm.	% on green weight	% of Total
1	28	200	240	2.61	7.25	1	54	202	242	2.56	7.91
2	33	405	486	5.29	14.7	3	15	403	483	5.09	15.8
3	47	605	726	7.92	21.9	4	39	603	723	7.64	23.6
5	10	804	964	10.5	29.1	6	30	814	976	10.3	31.9
6	45	1000	1193	13.0	36.1	8	32	1016	1218	12.9	39.8
8	45	1204	1437	15.6	43.4	10	54	1218	1460	15.4	47.7
11	13	1404	1677	18.3	50.7	13	35	1422	1704	18.0	55.6
13	58	1606	1919	20.9	58.0	17	30	1645	1971	20.8	64.4
17	08	1798	2149	23.4	65.0	22	00	1842	2207	23.3	72.2
21	35	1997	2387	26.0	72.3	27	53	2043	2448	25.9	76.8
27	22	2200	2630	28.7	79.5	35	05	2221	2661	28.1	87.0
34	35	2392	2860	31.1	86.5	48	52	2416	2895	30.6	94.5
47	48	2594	3102	33.8	93.7	69	50	2556	3063	32.4	100.0
69	25	2766	3308	36.1	100.0						

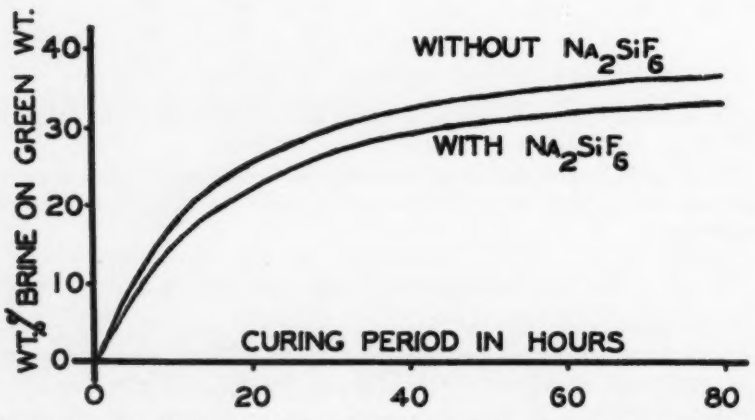

FIGURE 5.—The Effect of Sodium Silicofluoride upon the Flow of Brine from Wet-Salted Hides.

The greater amount of water thus retained by the hides treated with sodium silicofluoride is also saturated with salt, hence the salt up-take of these pieces is somewhat higher than for the controls. This work therefore confirms on a different basis the findings of Kritzinger[8] and shows that the difference in shrinkage is due to a greater loss of water from hides not treated with silicofluoride. Kritzinger reasoned that part of the difference was due to the re-

tention of insoluble sodium silicofluoride by the hide, but it is also clear now from the above work that the greater proportion of the difference is due to the retention of water by the stock.

TABLE IX

Shrinkage and Water Loss in Hides Cured for Three Days (With and Without The Addition of Sodium Silicofluoride)
(All percentages calculated on green weight)

	With sodium silicofluoride	Control
% Shrinkage	19.9	23.3
% Salt absorbed by hide	10.6	9.9
% Water collected	24.6	27.4
% Water retained by salt	4.33	3.87
% Water evaporated	1.57	1.95
% Total water lost by hides	30.5	33.22

It is difficult at this stage to give reasons why sodium silicofluoride should act in this manner. But it seems reasonable to suggest that the mild acidity imparted to the hides by the sodium silicofluoride would result in their swelling slightly, thus retaining moisture which would otherwise have been lost. Sodium silicofluoride is a hydrotropic agent, and through its action on the proteins would bring about such a stronger affinity for water.

Despite the fact that silicofluoride treated stock yields less brine than controls, it is significant to note from Table X and Figure 6 that such stock loses more nitrogen in the brine, despite the absence of any bacterial breakdown and solubilization of protein substance, during the first 30 hours of curing.

This greater removal of nitrogen during the early stages of curing can probably be ascribed to a better removal of blood from the bloodvessels. It was observed in the brine samples that the colour of those from the silicofluoride pieces was always darker than for the controls. Again this might be due to the slight acidity of this compound, which would tend to break down the blood [1]. It must also be borne in mind that sodium silicofluoride has the ability to disperse and remove globular proteins [5] from the stock, and that this will show up while the brine flow is strong enough. Towards the end of curing, after 30 hours, the control sample begins to show the influence of bacterial action upon the proteins, insofar as the nitrogen content of the brine begins to increase appreciably, whilst it remains more or less uniform yet for the silicofluoride series.

TABLE X

The Effect of Sodium Silicofluoride in the Salt upon the Nitrogen present in Brine Flowing from Wet-Salted Hides

Treatment:		2% Na_2SiF_6 in salt				Control	
Time Hrs.	Min.	% N in each aliquot	% Total nitrogen	Time Hrs.	Min.	% N in each aliquot	% Total nitrogen
1	54	.0405	.041	1	28	.0401	.040
3	15	.0327	.073	2	33	.0347	.075
4	39	.0280	.101	3	47	.0301	.105
6	30	.0273	.129	5	10	.0252	.131
8	32	.0253	.154	6	45	.0232	.154
10	54	.0238	.178	8	45	.0221	.176
13	35	.0226	.199	11	13	.0203	.196
17	30	.0234	.223	13	58	.0200	.216
22	00	.0200	.243	17	08	.0185	.235
27	53	.0201	.263	21	35	.0184	.253
35	05	.0176	.280	27	22	.0190	.272
48	52	.0200	.300	34	35	.0182	.291
69	50	.0160	.316	47	48	.0207	.311
				69	25	.0204	.332

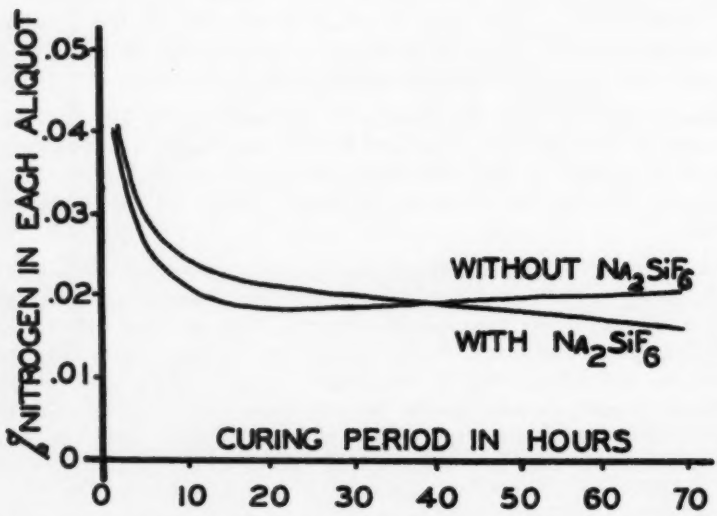

FIGURE 6.—The Effect of Sodium Silicofluoride upon the Nitrogen Present in Brine Flowing from Wet-Salted Hides.

Summary

A series of experiments, designed to obtain information on various factors influencing the rate of brine-flow and nitrogen removal from wet-salted hides, has enabled the following conclusions to be reached.

1. Washed hides tend to yield more brine, due to the excess surface moisture, but the salt is also absorbed to a slightly greater extent, resulting in less loss of weight from the green to the cured state.

2. In unwashed hides a large amount of nitrogen is removed in the brine, most of this nitrogen being representative of blood proteins.

3. Pressure upon hide stacks results in more brine flowing away under the experimental conditions employed.

4. Hides under pressure release more nitrogen in the brine.

5. When 2% sodium silicofluoride is added to the salt, less brine flows off the hides, hence the shrinkage is lower than for control hides.

6. Sodium silicofluoride appears to remove more blood from the hides than salt alone.

7. When hides are well washed prior to salting, only about 0.4% of the total hide nitrogen is removed with the brine flowing away from the stacks.

References

1. Harrow, B., Textbook of Biochemistry, 2nd Ed. W. B. Saunders Co., London, 1941.
2. Hausam, W., *Collegium*, **806**, 323 (1937).
3. ——, *ibid*, **814**, 55 (1938).
4. ——, *ibid*, **824**, 625 (1938).
5. Kritzinger, C. C., *Leather Ind. Research Inst., Res. Bull.* No. 12, 1945.
6. ——, *J. Am. Leather Chemists Assoc.*, **43**, 351 (1948).
7. ——, *ibid*, **44**, 216 (1949).
8. ——, *ibid*, **46**, 445 (1951).
9. McLaughlin, G. D., and Theis, E. R., *Collegium*, **678**, 431 (1926).
10. Stather, F. and Herfeld, H., *ibid*, **768**, 166 (1934).
11. ——, ——, *ibid*, **774**, 512 (1934).
12. ——, ——, *ibid*, **783**, 333 (1935).
13. ——, ——, *ibid*, **803**, 129 (1937).
14. van Zyl, J. H. M., *Leather Ind. Research Inst., Res. Bull.* No. 108, 1951.

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Canaigre Investigations

XI. Canaigre Root Tannin Makes Serviceable Leather*

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Previous papers on canaigre[1,2,3,4,5,6,7,8,9,10] have reported various phases of the culture, analysis and extraction of the roots and on the production of canaigre-tanned leather by small scale tanning tests. The present paper deals with the production of enough canaigre-tanned leather for a practical wear test and the results obtained in that test.

There is a growing shortage of tanning materials in this country. The chestnut blight will eventually cause a shortage of the most important domestic tanning material. The development of canaigre as a tanning material is one of the attempts to remedy this situation. Canaigre has advantages over many other materials in that it contains a large amount of tannin, usually about 30 per cent (moisture-free basis), and that it may be grown as an annual or biennial crop instead of requiring many years of growth before utilization, as is the case with barks or woods. There are difficulties in the extraction of this material because of the presence of starch and some objections to its use in tanning because of the rather low purity of its tannin. Means for overcoming these difficulties have been described in previous papers.

The ultimate test of a tanning material must be a large scale test in a commercial tannery using standard methods. The large tonnage of canaigre extract necessary for such a test is not yet available; however, sufficient extract[7] was available to tan enough sole leather for a practical wear test by about 70 individuals. Mail carriers were selected as suitable "guinea pigs" for this test because they wear their shoes for long distances every day in all sorts of weather and because, by proper selection of the post offices, the shoes would be available for frequent inspections by laboratory personnel.

Tannage of Leather

The leathers used in this test were tanned from croupons or double bends. For comparison, a single bend from each croupon was tanned in a commercial tannery by its regular process, and the other single bend from the same croupon was tanned at the Eastern Regional Research Laboratory with a blend containing canaigre extract. The analysis of the extract is shown in Table I.

*Presented at the 49th annual meeting, Cincinnati, Ohio, June 10, 1953.

** One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

TABLE I

Analysis of Canaigre Extract Used

	Per Cent
Total solids	95.2
Soluble solids	92.1
Insolubles	3.1
Nontannin	31.7
Tannin	60.4
Purity tan/sol. sol.	65.6
Total sugars	9.3
Reducing sugars	0.2

After the usual beamhouse treatment at the commercial tannery, 20 croupons were split along the backbone into single bends. Sixteen bends from the animal's right sides were tanned at the tannery by a commercial process using the usual commercial tanning blend. The remaining 24 bends were returned to the laboratory. These consisted of 16 left-side bends corresponding to the 16 right-side bends tanned at the tannery and 8 other bends, 4 left and 4 right. These 8 bends were used for a preliminary tannage, to partially mellow the liquors for the remaining bends.

The liquors used for the canaigre tannage at the laboratory were blends of 50 per cent canaigre, 25 per cent chestnut and 25 per cent sulfited quebracho liquors, calculated on a tannin basis. The vats held 3 single bends; the liquor to hide ratio was 8 to 1. A countercurrent press system of tannage was used, as similar as possible to that used in practice. The system was operated in such a manner that tail liquors contained 0.5 per cent tannin and the final head liquor 9 per cent. The tannage period was 6 weeks.

After the tannage at the laboratory, the leather was returned to the tannery, where all bends were finished simultaneously. All were then returned to the laboratory. Comparison of the canaigre and control leathers showed that the yield of the canaigre leather was slightly higher than that of the control leather, and the thickness somewhat greater. The yields calculated from weight to finished weight were 70.7 per cent for the control bends and 73.3 per cent for the comparable canaigre bends. In comparing these with normal tannery yields, it should be kept in mind that these yields were obtained on the bend portions only. Thickness was measured at 20 selected points on each bend. The average thickness of the control bends was 8.5 irons; for the comparable canaigre bends it was 8.8 irons. Several practical tanners ex-expressed the opinion that all leathers were entirely satisfactory in every respect.

Preparation of Test Shoes

The bends were matched into pairs; one that had been tanned at the tannery, the other from the same hide tanned at the laboratory with the canaigre

blend. Alternate right and left shoes were cut from each bend in such a way that a right sole was always matched with a left sole from a corresponding position on the bend from the opposite side of the animal. The thickness of each sole was measured. Each pair of soles was then numbered and stamped for permanent identification, and each pair was reserved for one pair of shoes. The soles, with the size specification for each pair, were then sent to a shoe factory, where low-cut, Garrison-type shoes were made for the test. Included in this test were pairs of insoles for a test of alum retannage. A report on these insoles will be given later.

The Shoe Service Test

The shoes were distributed to the carriers in four post offices near the laboratory—the Chestnut Hill and Germantown Offices in Philadelphia and the Glenside and Hatboro Offices in nearby Montgomery County. Each carrier recorded the time of wear, miles traveled and other data as to comfort of shoes, etc. The shoes were inspected each week by laboratory personnel. When a hole appeared in either sole, the men ceased wearing the shoes, which were returned to the laboratory for resoling.

As some of the men left the mail service before the test was completed, only 65 pairs of shoes were returned for resoling and only 62 pairs were returned at the end of the test.

In resoling, the canaigre test sole was placed on the shoe opposite to that used for the first part of the test. This eliminated to a large degree the effect caused by greater wear on one shoe than the other. After a hole appeared in either of the second soles, the test for canaigre was considered complete, and all soles were removed for testing and analysis.

Evaluation of Results

The results were evaluated in two ways. The first consisted of a comparison of soles that failed first (Table II). To obtain a fair comparison of the canaigre and control soles, it was assumed that the soles showing equal wear should be divided equally between canaigre and control. This gave columns D and E. For the sum of the two tests, this showed 66 in favor of the canaigre and 61 in favor of the control, indicating a slight but possibly not significant superiority of the canaigre soles.

TABLE II

Relative Wear Based on Number of Soles Showing First Indication of Failure

	A Canaigre Superior	B Control Superior	C Equal Wear	D A + ½ C	E B + ½ C
First half of test	17	9	39	36½	28½
Second half of test	14	17	31	29½	32½
Total	31	26	70	66	61

This method does not take into account difference in wear between right and left feet in some individuals. To make allowance for this, all pairs of shoes were separated into the following seven categories. The wearing of the initial soles was taken as the first half of the test, and the wearing of the resoles as the second half.

1. In each half of the test, right and left shoes failed at the same time—13 pairs.
2. In each half, the right sole was better—12 pairs.
3. In each half, the left sole was better—8 pairs.
4. In each half, the canaigre sole was better—7 pairs.
5. In each half, the control sole was better—3 pairs.
6. In one half, the canaigre was better and in the other half both soles failed at the same time—8 pairs.
7. In one half the control was better and in the other half both soles failed at the same time—11 pairs.

Category 1 indicates equal wear of leathers; 4 and 6 indicate superiority of canaigre soles; 5 and 7 indicate superiority of control soles; in categories 2 and 3 any differences between the types of leather are obscured by the difference in wear between right and left feet. Table III shows the results. There are discrepancies between results in Table II and those in Table III because, for several reasons, some of the shoes worn in the first half of the test were not worn in the second half. Table III indicates a slight but hardly significant superiority of the canaigre over the control soles.

TABLE III

Relative Wear Based on Comparison of Failures in Each Half of Test

	Category	Number of Pairs
Equal wear of each type of leather in each half	1	13
Canaigre sole superior	4–6	15
Control sole superior	5–7	14
Indeterminate	2–3	20

In the second method of evaluation, the durability was measured by the loss in thickness during wear. The thickness of the worn sole was measured at the thinnest point. For soles not completely worn through, the thickness worn away was taken as the difference between the original thickness and the remaining thickness. For soles completely worn through, the remaining thickness was, of course, zero. The thickness worn away, however, cannot be taken as the original thickness. Confirming the work of Whitmore and Downing [11], [12], we have found that there is never complete abrasion throughout the entire

thickness. When a sole has worn down to a thickness of 0.05 to 0.10 cm., a hole will appear without further abrasion. Therefore, an arbitrary correction was made by subtracting 0.05 cm. from each measurement of soles completely worn through. The results (Tables IV, V and VI) show an average loss of thickness of 0.408 and 0.407 cm. for the first and second tests of canaigre soles, and 0.406 cm. for each test of the control soles. This difference is not considered significant. Although the correction for thickness of the soles completely worn through might be objected to as empirical, in this case it does not affect to any appreciable degree the comparison of the two types of leather.

TABLE IV

Wear of Soles
Loss in Thickness Measured in Thousandths of a Centimeter
Test I—Initial Soles

Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control
1	290	376	30	378	409	57	435	434
2	353	319	31	176	280	58	451	340
5	409	406	32	233	397	59	497	465
6	389	381	33	410	442	60	515	452
7	372	403	36	410	273	61	360	369
9	355	387	37	514	384	62	448	294
10	330	422	38	487	497	63	436	398
11	394	380	39	436	512	64	443	440
12	354	361	40	513	363	65	324	423
13	432	367	41	472	361	66	413	393
15	421	267	42	444	410	67	453	309
16	439	407	43	394	384	68	416	455
17	426	419	44	464	468	69	401	411
18	528	431	46	509	538	70	367	503
19	454	412	48	491	476	73	463	409
21	507	460	50	325	330	74	265	465
23	441	408	51	487	396	75	480	471
24	436	441	52	318	391	77	398	452
26	430	406	53	502	500	78	359	356
27	450	274	54	413	381	79	465	455
28	234	400	55	401	408	80	367	508
29	250	451	56	377	408			
					Total		26544	26388
					Average		408	406

A record of the number of hours the shoes were worn and the mileage covered was obtained. There was little correlation between these. The mileage was the distance covered on deliveries, whereas the hours covered the total time worn, including time for sorting. It would be difficult to estimate the

TABLE V

Wear of Soles
Loss in Thickess in Thousandths of a Centimeter
Test II—Resoles

Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control	Shoe No.	Canaigre	Control
1	184	429	30	403	512	56	439	306
2	396	300	31	448	457	57	409	428
6	462	471	32	445	325	58	291	503
7	450	434	33	531	427	59	237	448
9	424	329	36	297	451	60	398	426
10	484	344	37	494	431	61	235	448
11	438	402	38	443	447	62	443	494
12	415	392	39	412	331	63	385	385
13	359	376	40	420	355	64	414	452
15	407	419	41	431	445	65	401	325
16	395	410	42	372	346	68	425	405
17	373	435	43	428	354	69	308	393
18	456	400	44	477	525	70	420	337
19	506	479	46	460	353	73	409	434
21	362	396	48	444	293	74	433	371
23	429	455	50	438	398	75	459	373
24	483	475	51	314	388	77	448	422
26	402	442	52	453	371	78	395	320
27	243	439	53	476	494	79	412	406
28	465	433	54	314	366	80	453	301
29	354	407	55	428	438			
					Total		25,229	25,151
					Average		407	406

TABLE VI

Summary of Tables IV and V
Average Thickness of Leather Worn Away

	Canaigre cm.	Control cm.
Initial soles	0.408	0.406
Resoles	0.407	0.406
Total	0.408	0.406

amount of wear on the shoes during the periods when no deliveries were being made.

There were large differences between individuals in the time required to wear out the soles and the mileage covered. The time of wearing ranged from 74 to 2130 hours, and the mileage from 100 to 1850 miles. The average time required was 320 hours, and the average mileage as reported was 290 miles.

For the reasons already given, it is believed that these figures are highly inaccurate and of little significance.

Although accurate records of hours worn and mileage covered would have been interesting, lack of these figures does not vitiate the results in any way, because the test was intended primarily to give a direct comparison of two types of leather used under the same conditions.

A record was made of the weight of the men in an attempt to correlate this with wear of the shoes. As expected, there was little correlation. Although the weight of the man may be one of the factors influencing wear, other factors are more important. For example, a man weighing 190 pounds wore his shoes without failure for 1196 hours, whereas a man weighing 135 pounds wore his shoes for only 206 hours without failure.

The figures obtained by the analyses of the original and worn leathers (Table VII) indicate that there is no significant difference between the analyses of the two original leathers. In comparing the analyses of the original and worn leathers, it must be kept in mind that the analysis of the worn leather is not that of the whole leather but only of that remaining after a large part of the thickness of the leather has been worn away from the grain side. This should have a tendency to increase the amount of hide substance and decrease the amount of combined tannin. As there is actually an increase in the amount of combined tannin, there is some indication that there has been a change resulting in a firmer combination of tannin and hide substance. The increase in insoluble ash and oil during wear is due to sand and tar picked up from driveways. There is a loss of soluble solids during wear.

TABLE VII

Analyses of Leathers

	Canaigre		Control	
	Before Wear	After Wear	Before Wear	After Wear
Oil, %	6.6	9.5	6.6	11.5
Insoluble ash, %	0.7	1.6	0.7	1.6
Hide substance, %	37.9	43.0	37.4	43.0
Soluble matter, %	30.4	18.5	30.7	17.5
Combined tannin, %	24.4	27.4	24.6	26.4
Total	100.0	100.0	100.0	100.0
Degree of tannage	64.4	64.0	65.6	61.7
Uncombined nontannin	19.9	8.8	19.2	8.5
Uncombined tannin	10.5	9.6	11.5	9.1
Glucose	5.8	2.3	5.2	2.2
Total ash	7.1	4.0	7.4	3.8
Epsom salts	7.8	2.9	8.9	2.3
pH	3.4	3.9	3.4	3.9

Almost all the men reported that the shoes were comfortable. A few complaints had no correlation with the type of leather used.

Conclusions

Within the limits of experimental error, the wear of leather tanned with a canaigre blend is equal to that of normally tanned leather.

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References

1. Canaigre Investigations IX. Laboratory Tannage of Heavy Leather. C. W. Beebe, W. S. Kip, II, and J. S. Rogers. *J. Amer. Leather Chemists Assoc.*, **46**, 197 (1951).
2. Canaigre Investigations III. An Improved Method of Extraction. T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **42**, 118 (1947).
3. Canaigre Investigations IV. Fermentation of Liquors for Production of High Purity Extracts. T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **42**, 128 (1947).
4. Canaigre Investigations VII. Fermentation of Extract Liquors and Identity of the Bacteria and Products of Their Growth. T. C. Cordon. *ibid*, **45**, 485 (1950).
5. Canaigre Investigations V. Analytical Studies on the Extraction of Canaigre Roots with Water and with Acetone–Water Mixtures. F. P. Luvisi and J. S. Rogers, *ibid*, **43**, 166, (1948).
6. Canaigre Investigations VI. Extraction with Organic Solvent-Water Solutions. F. P. Luvisi, T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **44**, 707 (1949).
7. Canaigre Investigations VIII. Preparation of Tanning Extracts by Continuous Countercurrent Extraction. R. M. Rieder, N. F. Roger, G. W. M. Phillips, and R. K. Eskew. *ibid*, **46**, 188 (1951).
8. Countercurrent Stationery Vat Leaching of Shredded Canaigre Roots. R. M. Rieder, V. A. Turkot, R. K. Eskew, and G. W. M. Phillips. *ibid*, **46**, 264, (1951).
9. Canaigre Investigations I. A Review and Preliminary Report. J. S. Rogers and G. A. Russell. *ibid*, **39**, 467 (1944).

10. Canaigre Investigations II. Dehydration of Bulk Lots of Canaigre Roots in the Locality Where Harvested. G. A. Russell, J. S. Rogers, and E. C. Stevenson. *ibid*, **39**, 479 (1944).
11. Practical Wearing Tests in Sole Leather. L. M. Whitmore and G. V. Downing. *ibid*, **37**, 150 (1942).
12. Note—Practical Wearing Tests in Sole Leather. L. M. Whitmore and G. V. Downing. *ibid*, **39**, 72 (1944).

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ABSTRACTS

Dyeing of Leather: Dyeing and Tannage. Charles Faure. *Bull. Assoc. Franc. Chimistes Inds. Cuir* **14**, 35 (1952). The relationship between charge on leather fiber (usually positive for chrome leather, weakly negative for vegetable leather, more strongly negative for syntan leather) and fixation of different types of dyes is reviewed. Vegetable leather possesses some affinity for acid dyes, probably because of free NH_2-groups, but syntan leather in general does not. Analogies in chemical structure between syntans and typical acid dyes are pointed out; both contain several aromatic nuclei and one or more SO_3Na-groups; they differ in that dyes possess chromophore groups and lack phenolic groups. The affinity of syntan leather for acid dyes increases as the number of SO_3Na-groups in the dye molecule decreases. Acid dyes containing OH-groups have less affinity for a syntan leather than those containing NH_2-groups. Finally some triphenylmethane dyes have fair affinity for syntan leather owing to their amphoteric character. When chrome leather is retanned with vegetable tannin or syntan, distributed uniformly throughout the leather, the leather will retain a slight positive charge and can be dyed without trouble, but if only the surface is retanned, acid dyes will penetrate. This can be overcome by treatment before dyeing with a cationic compound (Fixogen, Dermafix, Fixanol, etc.) to restore the positive charge. Penetration of a dye decreases with increasing molecular weight; for this reason it is impossible to obtain a true black that penetrates well. Penetration increases with number of SO_3Na-groups per dye molecule, and with decreasing difference in charge between leather and dye. While the relation between the charges on the leather and the dye molecule is of primary importance, the molecular structure of the dye must also be taken into account. H. B. M.

The Application of pH and rH in the Tannery. Charles Gastellu. *Bull. Assoc. Franc. Chimistes Inds. Cuir*, **14**, 45 (1952). The well-known applications of pH value are reviewed. The less familiar rH, a measure of the oxidation-reduction ("redox") potential of a solution, is discussed. Operations in the tannery where rH may be of importance include: unhairing with sulfides or other reducing agents, quinone tannage, vegetable tannage, oil tannage, and the fixation of tannins and stuffing greases on drying. Unfortunately the determination of rH in highly alkaline unhairing liquors, during oil tanning, or during drying, is difficult or even impossible, but the determination of rH of vegetable tan liquors is feasible. H. B. M.

The Object and Importance of the Hydroxyl Number. G. Blancher. *Bull. Assoc. Franc. Chimistes Inds. Cuir* **14**, 85 (1952). The determination of hydroxyl number is described. The determination is inaccurate if the acid number is high (over 110 for castor oil), and is not very precise when the hydroxyl number is low. Aldehydes and phenols interfere. The hydroxyl number is useful in identifying fatty acids obtained from oils, soaps or sulfonated oils; detection of higher alcohols or their esters; detection of suint; examination of surface-active agents, solvents and plasticizers. H. B. M.

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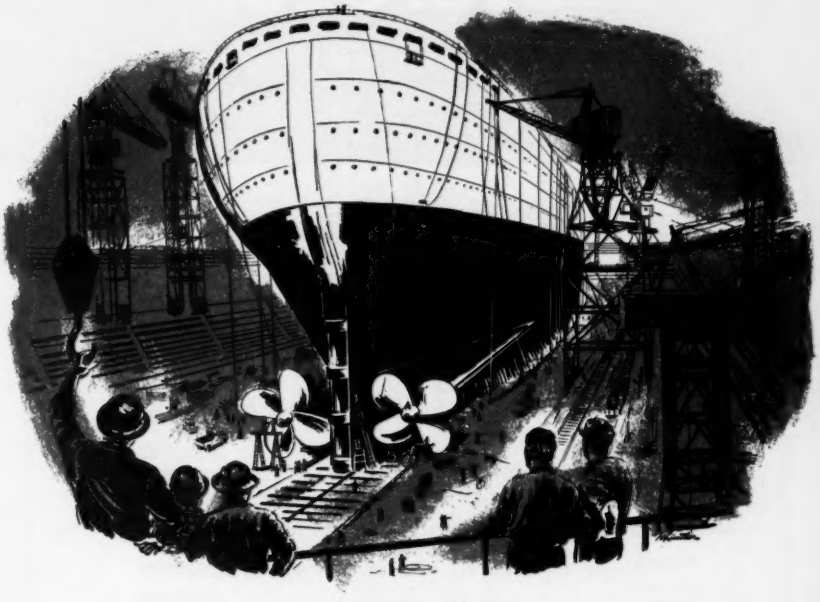

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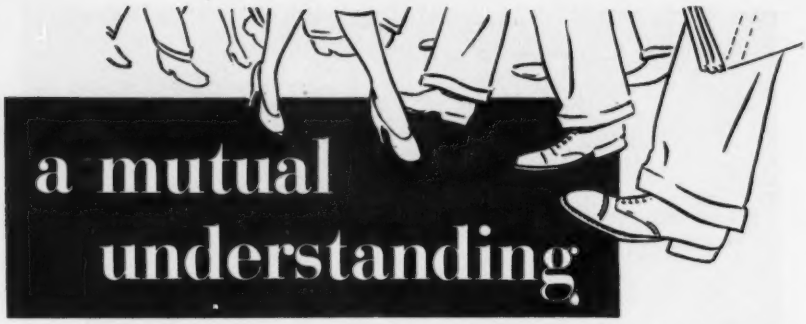

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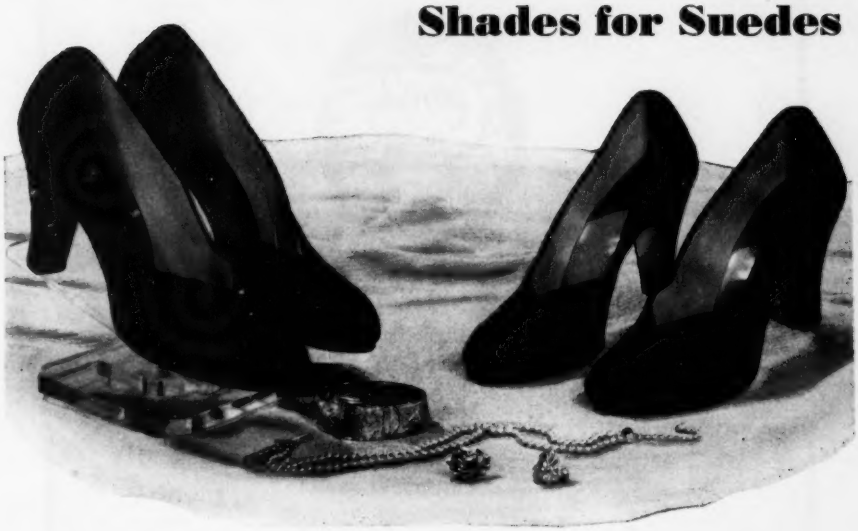

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INSOLUBLES	.65	.67	.7
WATER	15.98	6.71	6.7

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Also Available as Liquid with 30% Tannin

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